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INVESTIGATION OF THE ABSORPTION OF  
INFRARED RADIATION BY ATMOSPHERIC GASES

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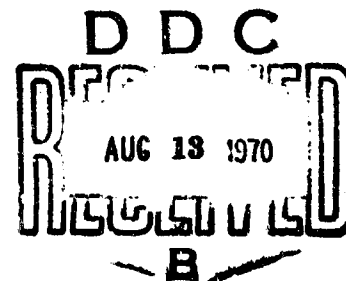
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# ABSTRACT

From spectral transmittance curves of very large samples of  $\text{CO}_2$  we have determined coefficients for intrinsic absorption and pressure-induced absorption from approximately  $1130\text{ cm}^{-1}$  to  $1835\text{ cm}^{-1}$ . Most of the pressure-induced absorption arises from the forbidden  $\nu_1$  and  $2\nu_2$  bands of the  $^{16}\text{C}^{12}\text{O}^{16}$  molecule, and the major portion of the intrinsic absorption arises from the same bands of the  $^{16}\text{C}^{12}\text{O}^{18}$  molecule. Curves of the absorption coefficients for samples of  $\text{CO}_2$  pressurized to approximately 10 atm, or more, with He are presented throughout most of the region from  $1885\text{ cm}^{-1}$  to  $2132\text{ cm}^{-1}$ . These curves and a table of the integrated absorption coefficient are adequate to determine the strengths of most of the bands of significance in this region. Spectral transmittance curves of  $\text{CO}_2$  absorption between approximately  $2065\text{ cm}^{-1}$  and  $2100\text{ cm}^{-1}$  are presented for a variety of samples. Curves of the pressure-induced absorption by  $\text{N}_2$  are presented for the  $2400\text{-}2650\text{ cm}^{-1}$  region.

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## SECTION 1

### SUMMARY AND DEFINITION OF TERMS

The absorption in atmospheric windows frequently cannot be treated by band-model methods which are applicable to spectral regions containing strong absorption bands. A significant portion of the attenuation in windows may result from continuum absorption due to the extreme wings of distant lines or to pressure-induced bands. The functional dependence of the continuum absorption on such parameters as path length, temperature, pressure, and atmospheric composition is quite different from that of line absorption. Laboratory studies of atmospheric gases under controlled conditions frequently are required to determine the portion of the absorption due to the continuum.

This report deals with a variety of situations in which continuum absorption and weak-line absorption are important. Section 2 deals with continuum absorption between approximately 2400 and 2650  $\text{cm}^{-1}$  due to a pressure-induced band of  $\text{N}_2$  and to the extreme wings of  $\text{CO}_2$  lines centered at lower wavenumbers. Pressure-induced bands and weak forbidden bands of  $\text{CO}_2$  in the 1100-2000  $\text{cm}^{-1}$  region are discussed in Section 3. By studying samples covering a wide range of pressures and path lengths, we have determined the contribution due to the continuum produced by the pressure-induced bands and that due to the weak bands which contain rotational line structure. We have been able to measure the  $\text{CO}_2$  absorption, even in the regions of very weak absorption near 1830  $\text{cm}^{-1}$  and 1130  $\text{cm}^{-1}$ .

Several  $\text{CO}_2$  bands which occur between 1890 and 2130  $\text{cm}^{-1}$  play a significant role in the absorption by long atmospheric paths. Section 4 includes experimental curves and tables from which the strengths of several of these bands can be determined. Also included in Section 4 are transmittance curves and tabulated results for several samples studied near 2080  $\text{cm}^{-1}$ .



A prominent feature in the spectrum near this wavenumber has proven to be useful in analyzing spectral curves obtained by aircraft. Section 5 contains a summary of experimental data which we have obtained previously and have recently put on magnetic tape. The tapes and a user's manual will be available in the near future for workers who need them.

All of the data included in this report are based on samples contained in one of two multiple-pass absorption cells which have been described previously.<sup>1</sup> The base lengths of the cells are approximately 29 m and 1 meter. Sample pressures up to 2.5 atmospheres are employed in the long cell; 21 atm is the maximum pressure used in the short cell.

The absorber thickness,  $u$ , of a gas sample is given by

$$\begin{aligned} u(\text{molecules/cm}^2) &= 2.69 \times 10^{19} p^*(\text{atm}) L(\text{cm}) (273/\theta) \\ &= 7.34 \times 10^{21} p^* L/\theta. \end{aligned} \quad (1-1)$$

The temperature  $\theta$  is in degrees Kelvin, and  $L$  is the geometrical path length through the sample. The density-equivalent-pressure  $p^*$  of the absorbing gas approaches its pressure  $p$  at low pressures. Because of the non-linear relationship between the density and the pressure of a gas,  $p^*$  may differ significantly from  $p$  at high pressures. For the gases and pressures used in the present investigation, the following expression is sufficiently accurate.

$$p^* = p(1 + c p) \quad (1-2)$$

The pressures are in atm and, near room temperature,  $c = 0.005$  for  $\text{N}_2\text{O}$  and  $\text{CO}_2$ , and  $0.001$  for  $\text{N}_2$  and  $\text{O}_2$ . For the largest sample of  $\text{CO}_2$ ,  $p^*$  is only approximately 11% greater than  $p$ ; in many of the samples the difference is negligible. In the following discussion certain quantities are said to be proportional to pressure; it should be borne in mind that the more correct quantity, density-equivalent pressure  $p^*$ , was used in the calculations where the difference between  $p^*$  and  $p$  was significant.

The true transmittance that would be observed with infinite resolving power is given by

$$T' = \exp(-u\kappa), \quad \text{or} \quad (-1/u) \ln T' = \kappa, \quad (1-3)$$

where  $\kappa$  is the absorption coefficient. Because of possible variations in  $\kappa$  with wavenumber and the finite slitwidth of a spectrometer, the observed transmittance  $T$  may differ from  $T'$  at the same wavenumber. The quantity  $T$  represents a weighted average of  $T'$  over the interval passed by the spectrometer.

Throughout this report we deal with three different basic types of absorption. In some spectral regions, an appreciable portion of the absorption is due to the extreme wings of lines whose centers are several  $\text{cm}^{-1}$  away. This wing absorption has the nature of a continuum, i.e., there is no structure, and because of the collision broadening of the lines, the absorption coefficient  $C_w$  due to the wing absorption is proportional to pressure. ( $C_w = C_w^0 p^*$ ) (See Eq. 1-6 and the discussion following it.)

Another type of continuum absorption arises from pressure-induced bands; the absorption coefficient,  $C_p$ , for pressure-induced absorption is also proportional to pressure. The absorption coefficient due to local lines whose centers occur within a few  $\text{cm}^{-1}$  of the point of observation is denoted by  $\kappa(\text{local})$ . The latter quantity may vary rapidly with wavenumber and depends on pressure because of collision-broadening of the absorption lines.

At a given wavenumber, there may be appreciable absorption due to local lines, the wing continuum, the pressure-induced continuum, or to any of these three. Therefore, the total absorption coefficient  $\kappa$  in Eq. (1-3) may be given by

$$\kappa = \kappa(\text{local}) + C_w + C_p. \quad (1-4)$$

For a sample of absorbing gas only, such as several of the  $\text{CO}_2$  samples discussed below, we can rewrite Eq. (1-4) as

$$\kappa = \kappa(\text{local}) + (C_{s,w}^0 + C_{s,p}^0) p^*, \quad (\text{absorbing gas only}) \quad (1-4a)$$

where the normalized coefficients  $C_{s,w}^0$  and  $C_{s,p}^0$  are the values of  $C_w$  and  $C_p$  respectively, when  $p^* = 1$ . The subscript  $s$  denotes self-broadening of the lines or self-induced absorption. Since  $u$  is proportional to  $pL$ ,  $(-L/T)$  due to wing continuum or pressure-induced continuum is proportional to  $p^2L$ .

We frequently are concerned with samples containing a non-absorbing gas, along with the absorbing gas. This gas broadens the absorption lines and may induce additional absorption by the pressure-induced bands of the absorbing gas. For a mixture of an absorbing gas and a broadening gas,

Eq. (1-4) becomes

$$\kappa = \kappa(\text{local}) + (C_{s,w}^0 + C_{s,p}^0) p^* + (C_{b,w}^0 + C_{b,p}^0) p_b^*. \quad (1-4b)$$

$C_{b,w}^0$  and  $C_{b,p}^0$  are the normalized coefficients for wing absorption and pressure-induced absorption by the absorbing gas due to the presence of the broadening gas denoted by subscript b.

The intrinsic absorption coefficient due to a single collision-broadened absorption line at a point within a few  $\text{cm}^{-1}$  of the line center,  $\nu_0$ , is given by the Lorentz shape:

$$k = \frac{S}{\pi} \frac{\alpha}{(\nu - \nu_0)^2 + \alpha^2}. \quad (1-5)$$

The line strength  $S = \int k d\nu$  is essentially independent of pressure for the conditions of the present study. It has been shown<sup>2,3</sup> that for  $|\nu - \nu_0|$  greater than a few  $\text{cm}^{-1}$ , the Lorentz equation may require modification by a factor of  $\chi$ , which is a function of  $(\nu - \nu_0)$ . Therefore, Eq. (1-5) becomes

$$k = k_L \chi = \frac{S}{\pi} \frac{\alpha \chi}{(\nu - \nu_0)^2 + \alpha^2} \quad (1-6)$$

where  $k_L$  denotes the value given by the Lorentz equation. The value of  $\chi$  is approximately equal to unity for small  $|\nu - \nu_0|$ , but may be as small as 0.01 for  $\text{CO}_2$  lines when  $(\nu - \nu_0)$  is as large as  $100 \text{ cm}^{-1}$ .

The half-width  $\alpha$  is proportional to pressure so that  $k$  is, in turn, proportional to pressure in the extreme wings where  $|\nu - \nu_0| \gg \alpha$ . Thus, the continuum absorption coefficient due to the extreme wings of many lines is proportional to pressure, as stated above.

## SECTION 2

### ATMOSPHERIC ABSORPTION BY $N_2$ BETWEEN 2400 AND 2600 $cm^{-1}$

The fundamental vibration band of  $N_2$  is centered near 2330  $cm^{-1}$  and produces measurable absorption from less than 2200  $cm^{-1}$  to more than 2600  $cm^{-1}$ . We have investigated the absorption by this band between approximately 2390  $cm^{-1}$  and 2650  $cm^{-1}$  because of its important role in atmospheric transmission in this region. Below 2390  $cm^{-1}$  the  $CO_2$  absorption in the atmosphere is much greater than the  $N_2$  absorption. The  $N_2$  band is pressure induced so that the probability of a transition in a given molecule is proportional to pressure, and the absorbance by a short path is proportional to  $p^2$ .

Shapiro and Gush<sup>4</sup> have published spectral data on  $N_2$  absorption for samples at approximately 20 atm pressure. Farmer et al<sup>5</sup> have also measured the absorption between 2400  $cm^{-1}$  and 2525  $cm^{-1}$  by approximately 1 atm of pure  $N_2$  with path lengths of a few hundred meters. The results of Farmer et al are consistent with the high-pressure data of Shapiro and Gush if  $(-ln T)$  is assumed to be proportional to  $p^2L$ , according to the discussion following Eq. (1-4a). The work reported here was undertaken to check the previous work and to determine the appropriate coefficient  $C_{0,p}^0$  for  $N_2$  absorption induced by  $O_2$ . From the value of this coefficient and the corresponding coefficient,  $C_{s,p}^0$ , for self-induced absorption by  $N_2$ , we have calculated the transmittance by  $N_2$  in the earth's atmosphere from approximately 2390  $cm^{-1}$  to 2650  $cm^{-1}$ .

Values of the absorber thickness of  $N_2$  were calculated by use of Eqs. (1-1) and (1-2). Since there is no absorption by  $N_2$  other than that which is pressure induced, Eqs. (1-3) and (1-4a) combine to give

$$-\frac{1}{u} \ln T = p^* C_{s,p}^o \quad (2-1)$$

for a pure  $N_2$  sample, and

$$-\frac{1}{u} \ln T = p^* C_{s,p}^o + p_{O_2}^* C_{O,p}^o \quad (2-1a)$$

for a sample of  $N_2 + O_2$ . Since the true transmittance  $T'$  changes slowly with wavenumber in continuum absorption, the observed transmittance  $T$  is essentially equal to  $T'$ . Note that  $C_{O,p}^o$  corresponds to absorption by  $N_2$  that is induced by  $O_2$ ; the  $O_2$  does not absorb. We detected no absorption by a sample of 8 atm of  $O_2$  with a 32.9 meter path length. After values of  $C_{s,p}^o$  had been found from pure  $N_2$  samples, we determined  $C_{O,p}^o$  from data on  $O_2 + N_2$  mixtures by use of Eq. (2-1a). The results for pure  $N_2$  and for  $O_2 + N_2$  mixtures are summarized in Fig. (2-1). The good agreement among the pure  $N_2$  data at different pressures provides evidence of the pressure dependence assumed in deriving Eq. (2-1). Below approximately  $2500 \text{ cm}^{-1}$ , our results for pure  $N_2$  differ by less than  $\pm 5\%$  from those by Shapiro and Gush.<sup>4</sup> At larger wavenumbers, the agreement is within the accuracy to which the curves of Shapiro and Gush can be read. Data obtained from samples of  $N_2$  with 5 atm of  $O_2$  compared well with data from samples of  $N_2$  with 8 atm of  $O_2$ , indicating the validity of the term involving  $p_b^*$  in Eq. (2-1a).

Air contains approximately 78 percent  $N_2$ , 21 percent  $O_2$ , and 1 percent other gases. Therefore, at  $296^\circ\text{K}$  and 1 atm pressure, there are  $0.78 \times 2.48 \times 10^{24} = 1.93 \times 10^{24}$  molecules of  $N_2/\text{cm}^2$  in a 1 kilometer path. From Fig. (2-1) we see that  $C_{O,p}^o \approx 0.95 C_{s,p}^o$ ; therefore, the "effective" pressure of 1 atm air is approximately 0.99 atm. It follows that  $(-\ln T)$  for a 1 km air path at 1 atm is  $0.99 \times 1.93 \times 10^{24} C_{s,p}^o$ . We have used this relationship along with the curve of  $C_{s,p}^o$  from Fig. (2-1) to calculate  $(-\ln T)$  versus wavenumber for 1 km of air. The results are plotted in Fig. (2-2).

Also shown for comparison in Fig. (2-2) is a curve corresponding to the continuum due to the extreme wings of the very strong  $CO_2$  lines centered between approximately  $2250 \text{ cm}^{-1}$  and  $2390 \text{ cm}^{-1}$ . This curve is based on data obtained in our laboratory and reported previously.<sup>2,6</sup>

Near  $2400 \text{ cm}^{-1}$ ,  $N_2$  and  $CO_2$  are seen to absorb approximately the same, but above  $2420 \text{ cm}^{-1}$  the  $N_2$  absorption is much greater. The upper curve represents both the  $N_2$  absorption and the  $CO_2$  wing absorption. The quantity  $(-\ln T)$  can be calculated for other pressures by making use of the knowledge that it is proportional to the square of the total pressure  $P$ . Some additional  $CO_2$  absorption not accounted for in Fig. (2-2) occurs because

of weak bands of the  $C^{12}O^{16}O^{18}$  and  $C^{12}O^{16}O^{17}$  isotopes and a pressure-induced band of the common isotope  $C^{12}O_2^{16}$ . (See Reference 6.)  $N_2O$  and  $H_2O$  also absorb in the spectral region covered in the figure with the strongest absorption by these two gases occurring above  $2500\text{ cm}^{-1}$ . Thus, the  $N_2$  absorption plays its most important role between  $2400\text{ cm}^{-1}$  and  $2500\text{ cm}^{-1}$ .

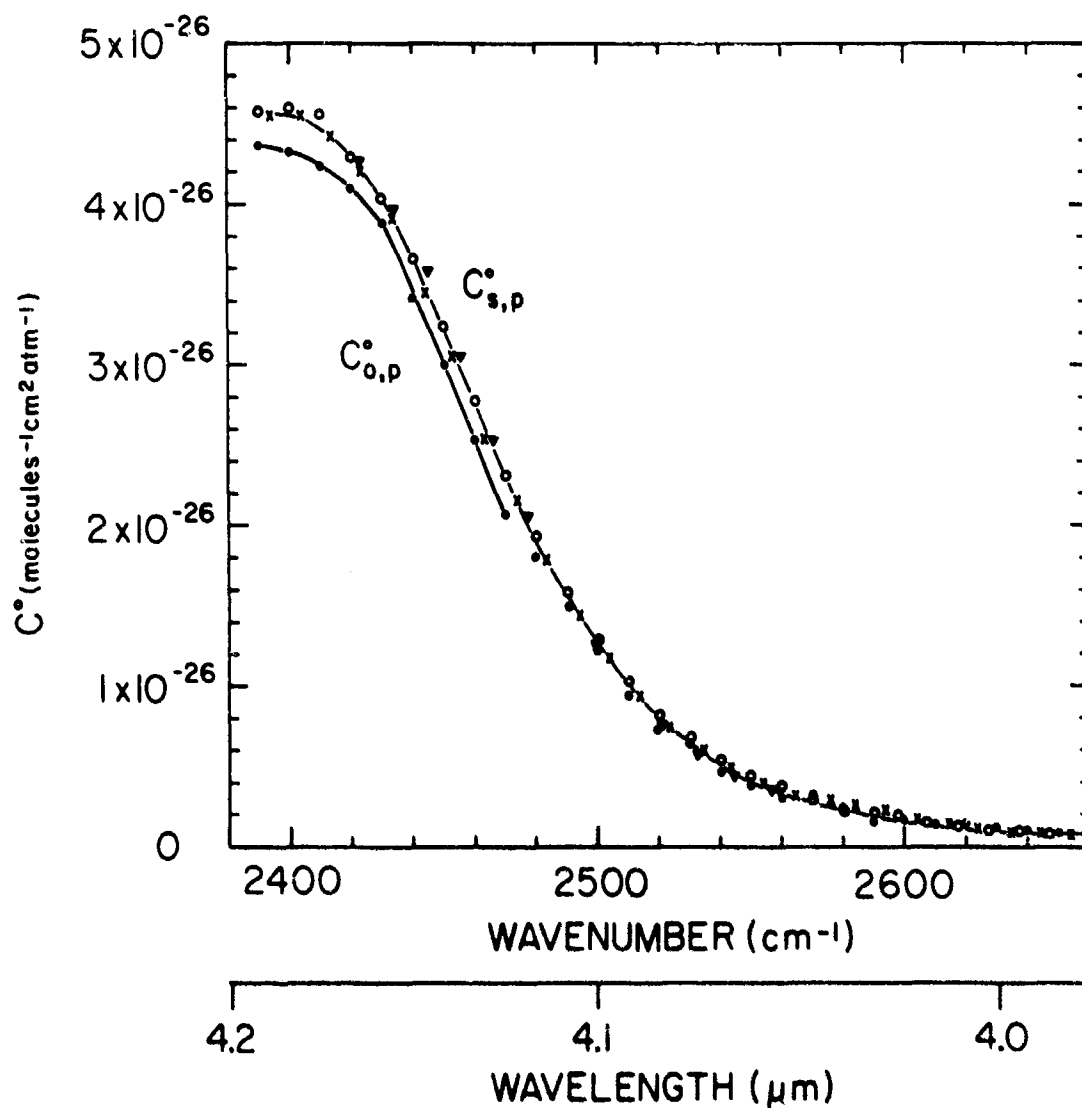


FIG. 2-1. Normalized Coefficients of Pressure-Induced  $\text{N}_2$  Absorption Plotted Versus Wavenumber. The upper curve represents  $C^\circ_{s,p}$  and is based on pure  $\text{N}_2$ . The various geometrical figures correspond to the following samples of pure  $\text{N}_2$ :  $\nabla$ ,  $L = 36.9$  m,  $p = 14.6$  atm;  $\times$ ,  $L = 32.9$  m,  $p = 13.6$  atm;  $\circ$ ,  $L = 32.9$  m,  $p = 21.8$  atm. The temperature is  $296^\circ\text{K}$ . The lower curve represents  $C^\circ_{o,p}$  and is based on mixtures of approximately 14 atm  $\text{N}_2 + 8$  atm  $\text{O}_2$  with  $L = 32.9$  m.

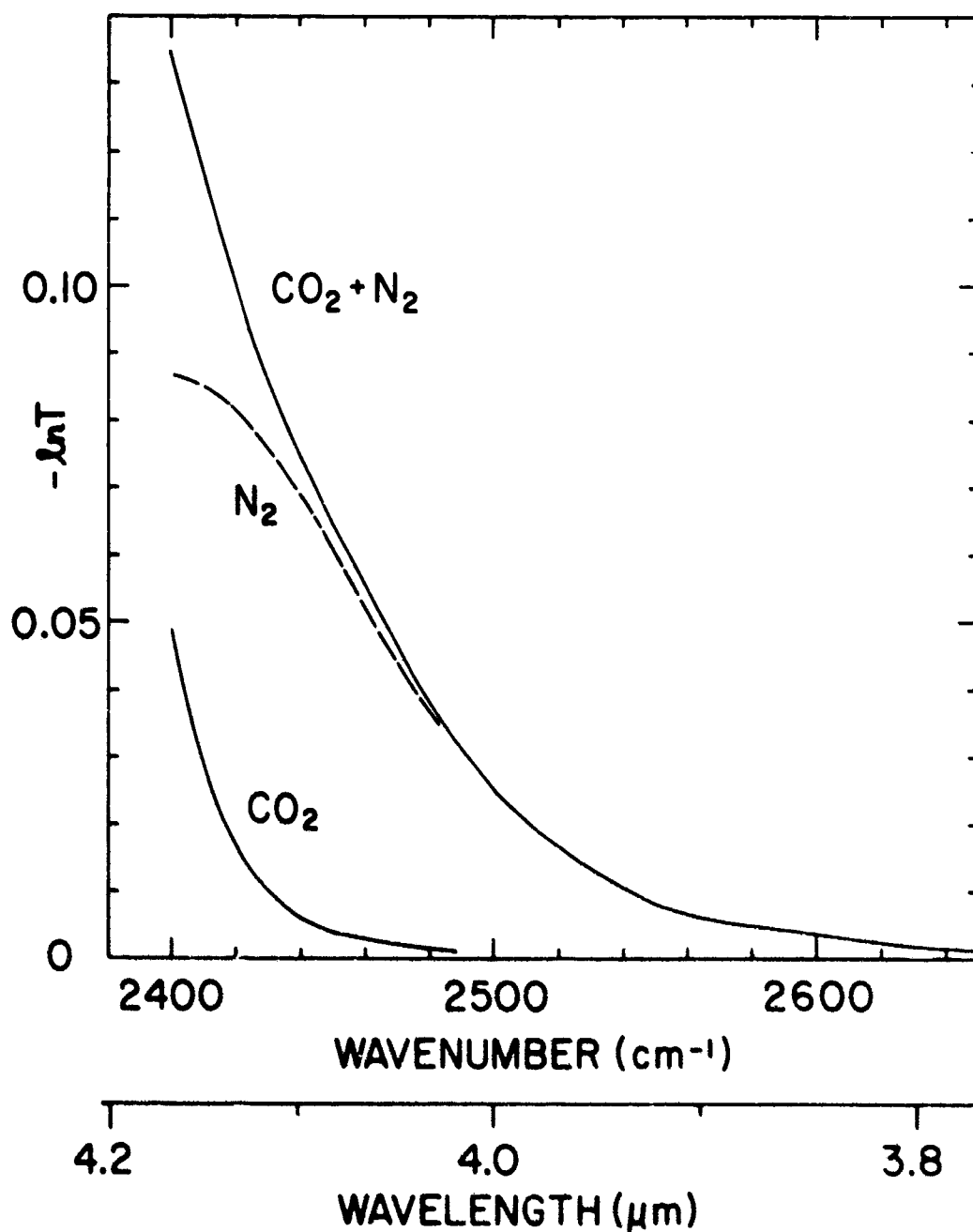


FIG. 2-2. Curves of  $-\ln T$  of N<sub>2</sub> and the Continuum Due to the Extreme Wings of CO<sub>2</sub> Lines. The curves correspond to a 1 km path of air at 296°K and 1 atm pressure.



### SECTION 3

#### ABSORPTION BY LARGE SAMPLES OF CO<sub>2</sub> BETWEEN 1100 AND 2000 cm<sup>-1</sup>

Absorption by CO<sub>2</sub> is relatively weak throughout the 1100 - 2000 cm<sup>-1</sup> (9.1 - 5 μm) region and has not been studied as thoroughly as most of the remainder of the spectrum. Figures 3-1, 3-2, and 3-3 show spectral transmittance curves for a variety of large samples at room temperature, 296°K. Some of the absorption is due to intrinsic bands, some to pressure-induced bands, and a small amount to wing absorption. From the transmittance maximum near 1130 cm<sup>-1</sup> to approximately 900 cm<sup>-1</sup>, most of the absorption is due to the bands involved in the well-known laser transitions. Several medium and strong bands occur between 2000 and 2400 cm<sup>-1</sup>; some of them are discussed in Section 4. Samples B and C represented in Fig. 3-3 are essentially opaque from 2020 cm<sup>-1</sup> to beyond 2400 cm<sup>-1</sup>. Data for the portions of the curves in Fig. 3-3 on either side of approximately 1590 cm<sup>-1</sup> were obtained at different times with different gratings in the spectrometer.

Most of the absorption between 1130 and 1500 cm<sup>-1</sup> is due to the ν<sub>1</sub> and 2ν<sub>2</sub> bands. The positions of the centers of these bands have been calculated for the four most common isotopes from the energy levels tabulated by Stull, Wyatt, and Plasse<sup>7</sup> and are listed in Table 3-1. Also listed are bands which have the same change in quantum numbers but arise from the lowest excited vibrational energy level. New notations for the identification of CO<sub>2</sub> energy levels and isotopes are described as footnotes of Table 3-1; the new notations are used hereafter. The bands listed are forbidden for the symmetric 626 and 636 molecules at low pressures; however, as the pressure increases, the interaction of the molecules with their neighbors disturbs the symmetry so that the transitions may occur. As discussed in Section 1, the absorption coefficient for these pressure-

TABLE 3-1

CENTERS OF CO<sub>2</sub> BANDS  
BETWEEN 1100 AND 1450 cm<sup>-1</sup><sup>a</sup>

Isotope <sup>b</sup>	(100,0) <sub>I</sub> <sup>c</sup> [10 <sup>0</sup> 0]	(100,0) <sub>II</sub> [02 <sup>0</sup> 0]	(110,1) <sub>I</sub> - (010,1) <sub>I</sub> [11 <sup>1</sup> 0-01 <sup>1</sup> 0]	(110,1) <sub>II</sub> - (010,1) <sub>I</sub> [03 <sup>1</sup> 0-01 <sup>1</sup> 0]
626	1388.20	1285.43	1409.45	1265.11
636	1370.11	1265.84	1388.65	1248.03
628	1365.89	1259.49	1386.93	1239.29
627	1376.03	1272.35	1397.28	1251.98

<sup>a</sup>Band centers are in cm<sup>-1</sup> and are based on energy levels tabulated by Stull, Wyatt, and Plass.<sup>7</sup>

<sup>b</sup>The number in the first column refers to the isotopic species. 626 corresponds to <sup>16</sup>C<sup>12</sup>O<sup>16</sup>, 636 to <sup>16</sup>C<sup>13</sup>O<sup>16</sup>, 628 to <sup>16</sup>C<sup>12</sup>O<sup>18</sup>, and 627 to <sup>16</sup>C<sup>12</sup>O<sup>17</sup>.

<sup>c</sup>The lower energy level is the ground state when only one level is given. Two different notations are given for the energy levels involved in the transitions. The notation in brackets is widely used. The other notation has certain advantages and is gaining acceptance. Since  $v_1 \approx 2v_2$  for CO<sub>2</sub>, the two energy levels 10<sup>0</sup>0 and 02<sup>0</sup>0 are approximately the same, as are 10<sup>0</sup>1 and 02<sup>0</sup>1, etc. In order to illustrate the relationship between the old and new notations, we consider the three energy levels given in the old notation by 20<sup>0</sup>3, 12<sup>0</sup>3, and 04<sup>0</sup>3. Note that quantum numbers  $v_3$  and  $L$  are both fixed and that  $2v_1 + v_2$  is constant. In the new notation the three levels become (203,0)<sub>I</sub>, (203,0)<sub>II</sub>, and (203,0)<sub>III</sub>. The Roman numeral subscript denotes the order in which the bands occur without regard to the assignment of  $v_1$  or  $v_2$ ; I denotes the highest wavenumber, II the second highest, etc. The first digit in the parenthesis is the largest value of  $v_1$  in a group; the second is the smallest value of  $v_2$ . The third digit is  $v_3$  and the one following the comma is  $L$ .

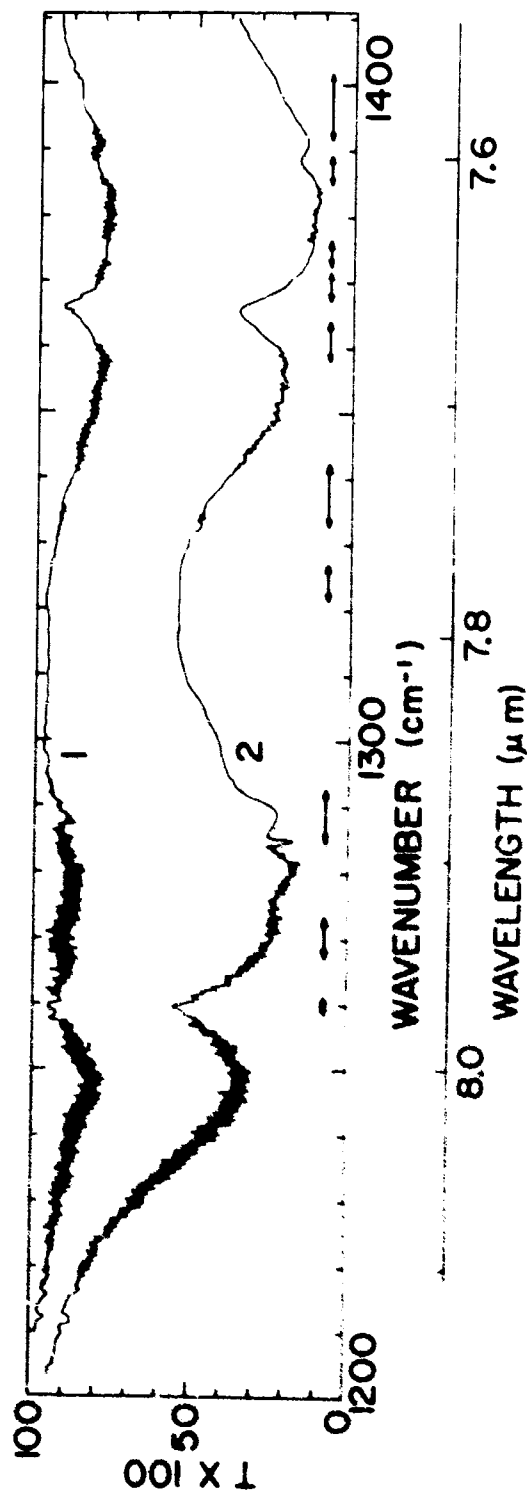


FIG. 3-1. Spectral Transmittance Curves of Two Relatively Low-Pressure Samples of  $\text{CO}_2$  Between  $1200$  and  $1400 \text{ cm}^{-1}$ . The spectral slitwidth varies from approximately  $0.45 \text{ cm}^{-1}$  at  $1200 \text{ cm}^{-1}$  to  $0.65$  at  $1400 \text{ cm}^{-1}$ . In some places where the  $\text{H}_2\text{O}$  absorption covered an area which included as many as 5 or 6  $\text{CO}_2$  lines, we made no attempt to reconstruct the  $\text{CO}_2$  structure. Instead a smooth line was drawn to represent the average  $\text{CO}_2$  transmittance. Intervals containing significant absorption by  $\text{H}_2\text{O}$  are indicated by arrows. The curves in this figure were obtained as part of a previous study<sup>8</sup> in our laboratory. The sample parameters are: Sample 1,  $p = 0.25 \text{ atm}$ ,  $L = 713 \text{ m}$ ; Sample 2,  $p = 1.05 \text{ atm}$ ,  $L = 359 \text{ m}$ .

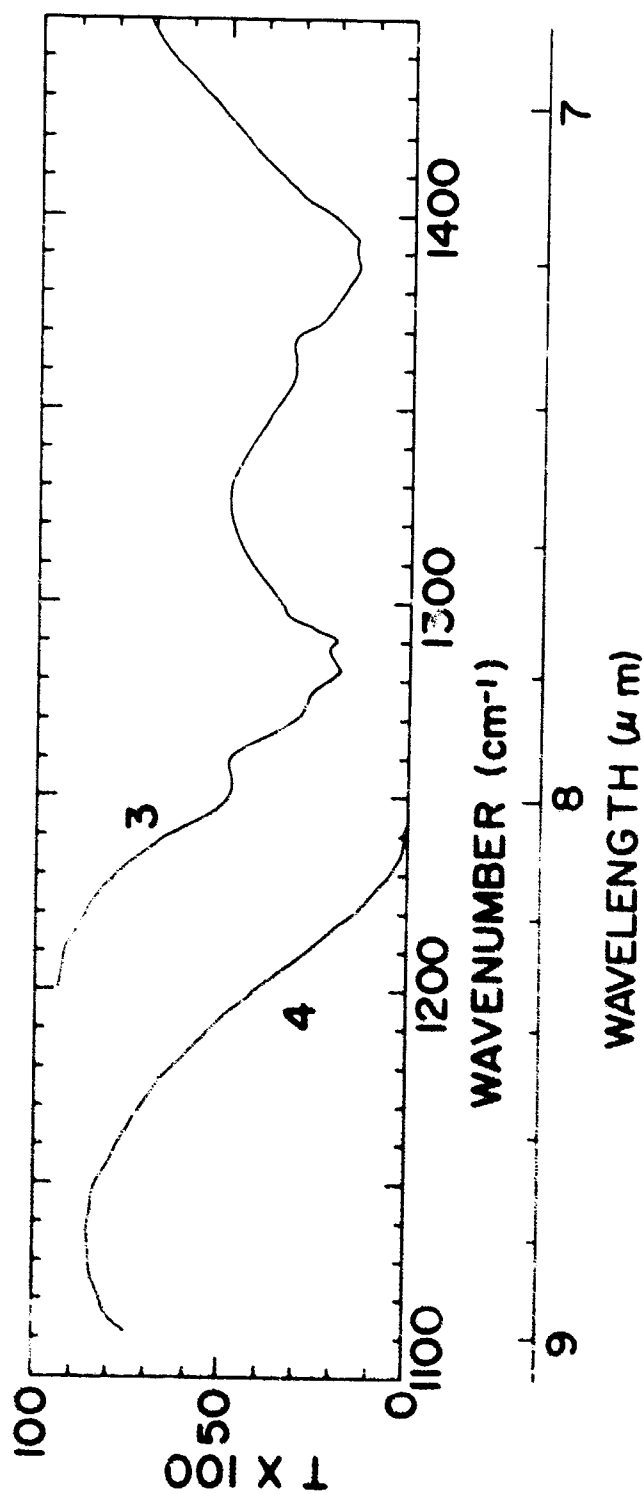


FIG. 3-2. Spectral Transmittance Curves of Two High-Pressure Samples of CO<sub>2</sub> Between 1100 and 1450 cm<sup>-1</sup>. The spectral slitwidth varies from approximately 2.0 cm<sup>-1</sup> at 1100 cm<sup>-1</sup> to 3.6 cm<sup>-1</sup> at 1450 cm<sup>-1</sup>. The sample parameters are: Sample 3, p = 3.70 atm, L = 32.9 m; Sample 4, p = 14.6 atm, L = 32.9 m.

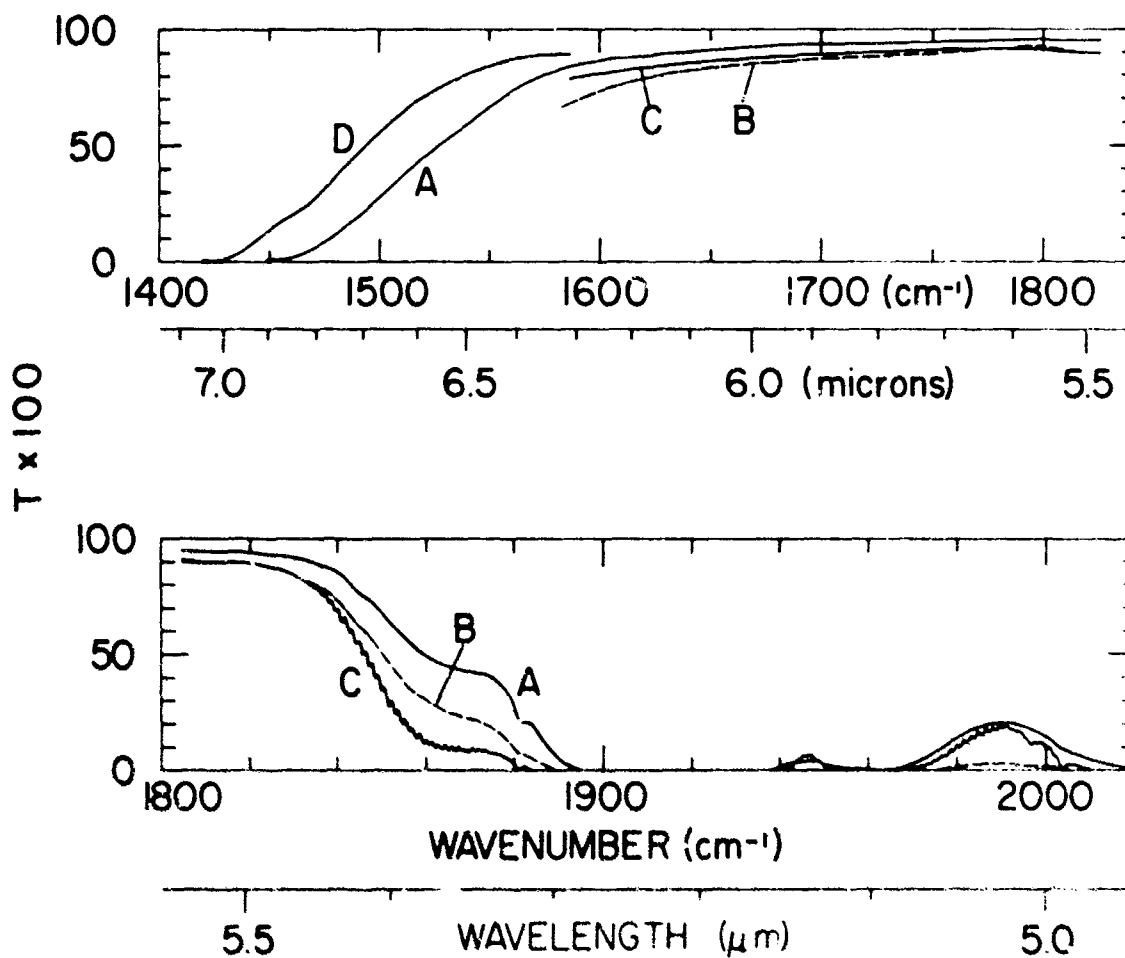


FIG. 3-3. Spectral Transmittance Curves from  $1400\text{ cm}^{-1}$  to  $2020\text{ cm}^{-1}$ . The spectral slitwidth varies from approximately  $0.55\text{ cm}^{-1}$  at  $1500\text{ cm}^{-1}$  to  $1.0\text{ cm}^{-1}$  at  $2000\text{ cm}^{-1}$ . The samples are pure  $\text{CO}_2$  and the parameters are:

<u>Sample</u>	<u>P</u> <u>(atm)</u>	<u>L</u> <u>(meters)</u>
A	14.6	32.9
B	21.3	32.9
C	2.35	933
D	1.82	1067

induced bands is proportional to  $p$ , and  $(- \ln T)$  is proportional to  $p^2 L$ . Because of the asymmetry of the 628 and 627 molecules, they can absorb at low pressures, and the dependence of their absorption on pressure and absorber thickness is similar to that of other intrinsic absorption bands. We expect the 628 bands to be approximately 10 times as strong as the corresponding 627 bands since the asymmetry of the former molecule is twice as much and the abundance is 5 times as great as that of the latter. Any absorption by one of these bands of the 626 molecule would be pressure-induced, and the ratio of its strength to that of the corresponding 626 band is probably about 1.1:99, the ratio of the abundances of  $C^{13}$  and  $C^{12}$ .

The strength of each difference band with  $(010,1)_I$  as the lower state is expected to be approximately 4 percent as great as the associated fundamental or overtone band which arises from the same change in quantum numbers. This relationship is based on the assumption that the strengths are proportional to the populations of the lower energy levels. At room temperature the population of the  $(010,1)_I$  level is approximately 4% of the  $(000,0)$  level.

On the basis of the above discussion, we expect most of the pressure-induced absorption to result from the  $(100,0)_I$  and  $(100,0)_{II}$  bands of the 626 molecule and the major portion of the intrinsic absorption to arise from the same bands of the 628 molecule. Furthermore, we expect the fraction of the absorption due to the pressure-induced bands to increase with increasing pressure. Figures 3-1 and 3-2 confirm these expectations. Sample 1, which has a relatively low pressure and long path, shows two distinct band centers near 1260 and 1366  $\text{cm}^{-1}$ , the calculated positions of the 628 band centers given in Table 3-1. Sample 3, which is at 3.70 atm shows transmittance minima near 1285 and 1388  $\text{cm}^{-1}$ , the calculated band centers for the 626 molecule. The 628 bands have been observed with relatively coarse resolution by Eggers and Arends<sup>9</sup> from samples enriched in  $O^{18}$ . The positions of the band centers determined by these workers agree with ours to less than the experimental uncertainties. The pressure-induced 626 bands have been observed by Welsh, Crawford, and Locke.<sup>10</sup>

The major errors result from errors in placing the zero-absorbance curves on the sample curves and from absorption by  $H_2O$  which appeared as an impurity in the  $CO_2$  in spite of efforts to keep it dry. Much of the  $H_2O$  absorption was accounted for before the curves were replotted by comparing the original sample curves with spectral curves of  $H_2O$  with  $N_2$  as a broadening gas. Spectral regions between 1100 and 1400  $\text{cm}^{-1}$  where  $H_2O$  absorption was partially accounted for are indicated by arrows in Fig. 3-1. The  $H_2O$  absorption was most serious between 1500 and 1800  $\text{cm}^{-1}$  because the  $H_2O$  lines are stronger and the  $CO_2$  absorption is weaker. The large amount of gas required for the long cell could not be purified as effectively as the smaller amount required to fill the short cell.

Furthermore, the absorption by  $H_2O$  is approximately proportional to the pressure of a mixture of constant composition while the pressure-induced  $CO_2$  absorption is proportional to the square of the pressure. Therefore, the  $H_2O$  absorption was less important for the high-pressure samples in the short cell than for the lower-pressure samples in the long cell.

In regions where there is intrinsic absorption due to local lines and pressure-induced absorption, but no wing absorption, Eq. (1-4a) reduces to

$$\kappa = \kappa(\text{local}) + C_{s,p} = \kappa(\text{local}) + C_{s,p}^0 p^*.$$

Since  $C_{s,p}$  is proportional to  $p^*$ , and  $\kappa(\text{local})$  is not, we have been able to determine each of these quantities from spectral curves of two or more samples at quite different pressures. At pressures less than a few atm,  $\kappa(\text{local})$  varies rapidly with wavenumber because of the line structure. Since the spectral slitwidth of the spectrometer was greater than the line widths at low pressures,  $\kappa(\text{local})$ , and thus  $\kappa$ , could not be measured directly at a given wavenumber. We were not interested in retaining all of the structure in the spectra, but in the values of the constants averaged over intervals approximately  $5\text{-}10\text{ cm}^{-1}$  wide. The strength,  $S = \int \kappa dv$ , of an intrinsic absorption line is independent of pressure; therefore, the average of  $\kappa(\text{local})$ , which may result from several neighboring lines, is essentially independent of pressure if the interval is several line widths wide and contains the centers of all the lines contributing to the absorption.

If we consider only the true transmittance of the local lines,  $(-1/u) \overline{\ln T'}(\text{local})$  is equivalent to  $\kappa(\text{local})$ . (The bar represents an average over wavenumber, and the prime denotes true transmittance that would be observed with infinite resolving power.) However, we do not read  $-\overline{\ln T'}$  from a spectral curve, but a slightly different quantity,  $-\overline{\ln T}$ , since we average the observed transmittance curve over a  $5\text{-}10\text{ cm}^{-1}$  interval. The difference between these two quantities decreases with wider lines and thus with increasing pressure; it also decreases with increasing average transmittance by the lines. We first assumed that  $\overline{\ln T} = \overline{\ln T'}(\text{local}) + \overline{\ln T'}(\text{continuum})$  and that  $(-1/u) \overline{\ln T}(\text{local}) = \overline{\kappa}(\text{local})$  in order to calculate  $C_{s,p}^0$  and an approximate value of  $\overline{\kappa}(\text{local})$  from data for two samples at different pressures. The approximate widths and spacings of the lines are known, so that by applying simple, band-model theory we were able to calculate a corrected  $\overline{\kappa}(\text{local})$  and to adjust the values of  $\overline{T}$ , which were then used to determine a corrected value of  $C_{s,p}^0$ . In most cases, there was less than 10% difference between  $(-1/u) \overline{\ln T}(\text{local})$  and  $(-1/u) \overline{\ln T'}(\text{local})$ , so that the remaining error due to the averaging was probably not more than a few percent after the correction was made.

Average values of the quantities were calculated throughout the 1100 - 1500  $\text{cm}^{-1}$  region for intervals 10  $\text{cm}^{-1}$  wide, except near the points of inflection where narrower intervals were used. The results are presented in Fig. 3-4. The uncertainty in the plotted values of  $\kappa(\text{local})$  and  $C_{s,p}^0$  is greater in regions where one of the quantities is changing rapidly. For example, there is extra uncertainty in the heights and positions of the peaks of the upper curve near 1275  $\text{cm}^{-1}$  and 1385  $\text{cm}^{-1}$  where the lower curve is steep.

The general shape of the upper curve in Fig. 3-4 is similar to that expected for the  $(100,0)_I$  and  $(100,0)_{II}$  intrinsic bands of the 628 molecule. The P- and R-branches are evident, and the band centers agree well with the calculated values given in Table 3-1. Because of the relatively coarse spectral resolution used in the calculations, the line structure apparent in Fig. 3-1 has been smoothed. Any obvious contribution by the same bands of the 627 isotope or by the difference bands of the 626 isotope is obscured by the coarse resolution and the scatter in the experimental points. However, these bands undoubtedly contribute to the absorption in accordance with the discussion near the beginning of this section. The integrated absorption coefficient for the intrinsic absorption by the local lines expressed in  $\text{molecules}^{-1} \text{cm}^2 \text{cm}^{-1}$  is  $43.9 \times 10^{-24}$  from 1200 to 1310  $\text{cm}^{-1}$ , and  $64.5 \times 10^{-24}$  from 1310 to 1420  $\text{cm}^{-1}$ . The estimated uncertainty is  $\pm 10$  percent.

The lower panel of Fig. 3-4 shows a spectral curve of the normalized absorption coefficient for pressure-induced absorption. The absorption peaks agree well with the calculated band centers 1285.43 and 1388.20  $\text{cm}^{-1}$ , given in Table 3-1 for the pressure-induced bands of the 626 isotope. The absorption by the 627 and 628 molecules probably have a pressure-induced component, but it is apparently much smaller than that by the 626 molecule. The two bands are seen to overlap and to produce measurable absorption over a wider spectral interval than that covered by the intrinsic bands illustrated in the upper panel. Except near the peak at 1388  $\text{cm}^{-1}$ , the data points corresponding to different samples agree within the expected experimental error. Below approximately 1130  $\text{cm}^{-1}$ , the continuum is influenced by the wings of the lines centered from about 1000  $\text{cm}^{-1}$  to 1100  $\text{cm}^{-1}$ .

The integrals of the normalized coefficients in  $\text{molecules}^{-1} \text{cm}^2 \text{atm}^{-1} \text{cm}^{-1}$  are  $67.3 \times 10^{-24}$  from 1130 to 1330  $\text{cm}^{-1}$  and  $101 \times 10^{-24}$  from 1330 to 1500  $\text{cm}^{-1}$ ; the estimated uncertainties are  $\pm 8$  percent. We note that the ratio of the integrals is approximately 3 to 2, the same as that for the corresponding intrinsic bands.

Curves of  $\kappa(\text{local})$  and  $C_s^0$  are shown in Fig. 3-5 for the region between 1490 and 1835  $\text{cm}^{-1}$ . Since not all the continuum is due to pressure-induced absorption, we have omitted the subscript p from  $C_s^0$  in Fig. 3-5. The symbol  $C_s^0$  is written without a p or w, which denote pressure-induced or



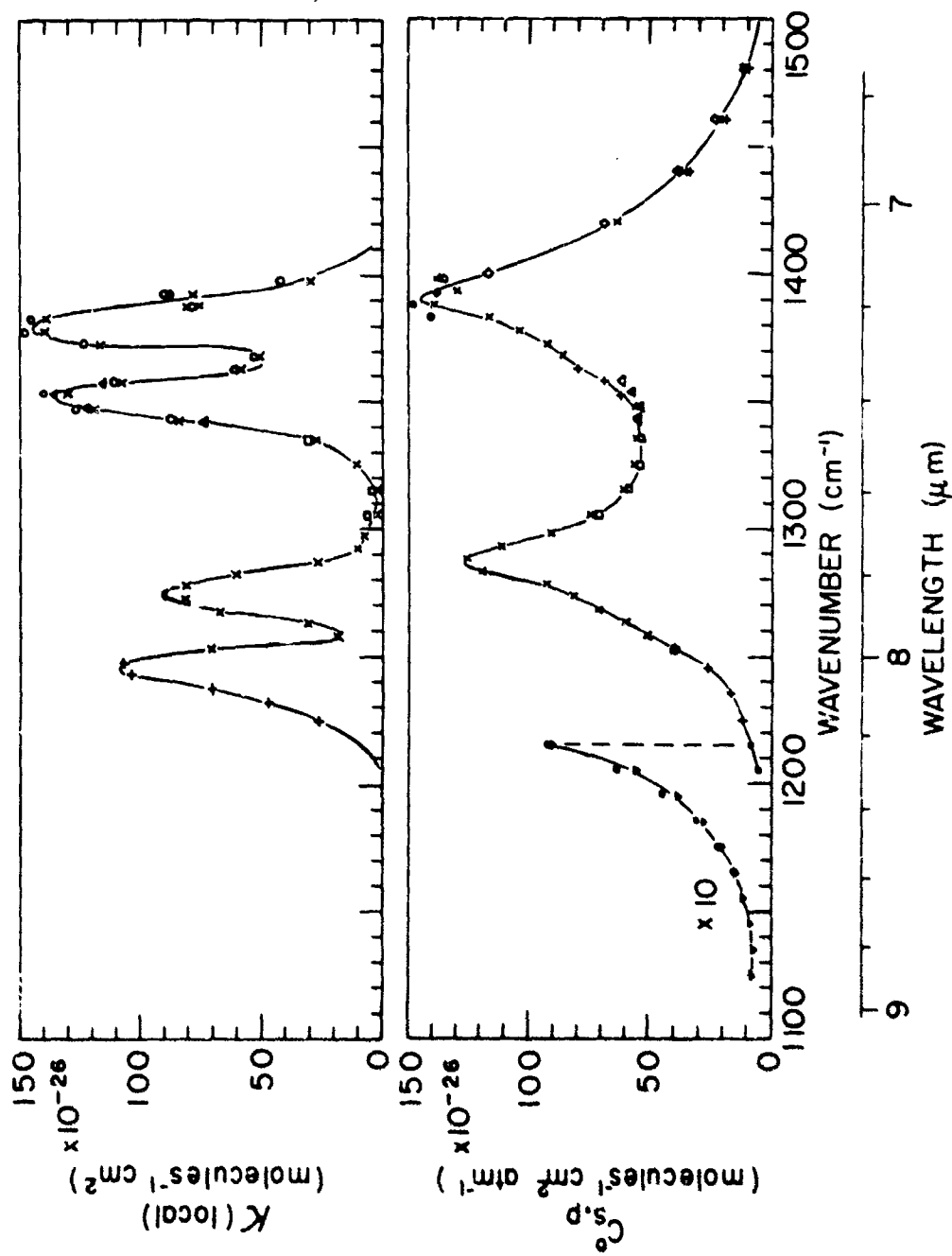


FIG. 3-4. Spectral Plots of  $\kappa(\text{local})$  and  $C_{s.p.}^0$  for Pure  $\text{CO}_2$  from 1100 to 1500  $\text{cm}^{-1}$ . Values of  $C_{s.p.}^0$  were multiplied by 10 before they were plotted to form the short curve below approximately 1215  $\text{cm}^{-1}$ .

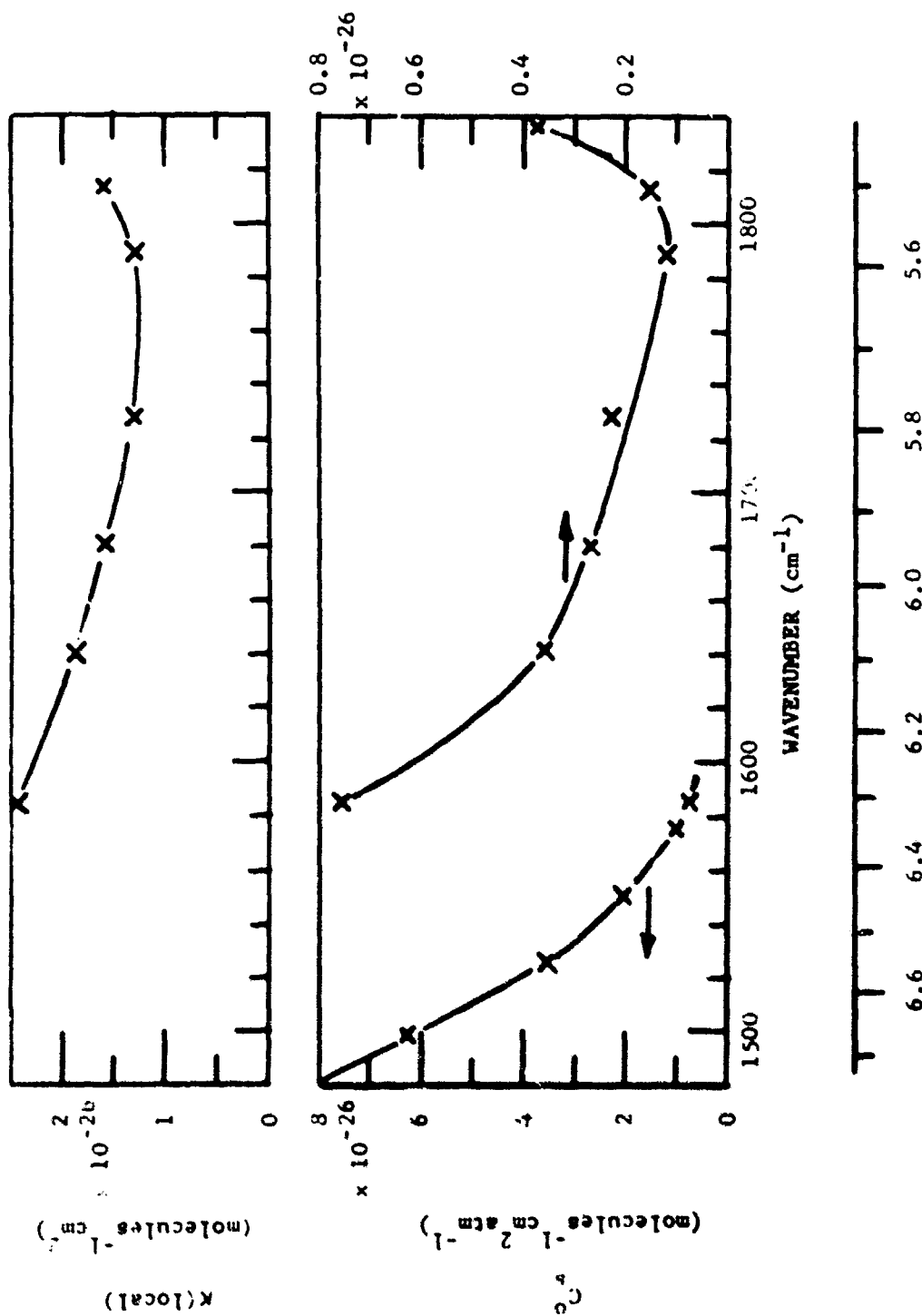


FIG. 1-5. Spectral plot of  $K(\text{local})$  and  $C_g$  for Pure  $\text{CO}_2$  from 1490 to 1835  $\text{cm}^{-1}$ . The upper curve is subject to considerable error and probably represents maximum values. Each curve in the lower panel is read from the ordinate scale indicated by the arrow. Some of the continuum absorption, particularly from 1790 to 1835  $\text{cm}^{-1}$ , probably results from the wings of lines centered at higher wavenumbers.

wing absorption, respectively, when the type of continuum is now known, or, in some cases, when it is clear which is being considered. The curve in the lower panel from 1490 to 1590  $\text{cm}^{-1}$  is based primarily on Samples A and D whose transmittance curves are shown in Fig. 3-3. Samples B and C form the bases for the curves in Fig. 3-5 above 1585  $\text{cm}^{-1}$ . The most serious errors between 1490 and 1850  $\text{cm}^{-1}$  arise from absorption by the  $\text{H}_2\text{O}$  impurity. Near the  $\text{H}_2\text{O}$  band center at approximately 1585  $\text{cm}^{-1}$ , the  $\text{H}_2\text{O}$  absorption is less than on either side. At this point the estimated error in  $C_s^0$  is between 0.1 and 0.2  $\times 10^{-26}$  molecules $^{-1}$   $\text{cm}^2$  atm $^{-1}$ . At other points between 1490 and 1585  $\text{cm}^{-1}$ , the errors may be twice this large.

Near 1788  $\text{cm}^{-1}$  the  $\text{H}_2\text{O}$  absorption is still bothersome, but it is much less than at most places between there and 1585  $\text{cm}^{-1}$ . The estimated absorptance by the  $\text{H}_2\text{O}$  impurity in Sample B was approximately 2 percent, while that by the  $\text{CO}_2$  was 8 percent. We also attempted to account for the  $\text{H}_2\text{O}$  absorption in Samples B and C at three other points between 1788 and 1590  $\text{cm}^{-1}$ . These points were chosen between  $\text{H}_2\text{O}$  lines where the  $\text{H}_2\text{O}$  absorption was less than at any other point within several  $\text{cm}^{-1}$ . The estimated correction for  $\text{H}_2\text{O}$  absorptance was less than 5 percent at these points for B, the 21.3 atm sample contained in the shorter absorption cell. The correction for  $\text{H}_2\text{O}$  absorptance was as much as 10 percent to 15 percent at these same points for Sample C. At 1783  $\text{cm}^{-1}$  the estimated uncertainty in the plot of  $C_s^0$  is 0.05  $\times 10^{-26}$  molecules $^{-1}$   $\text{cm}^2$  atm $^{-1}$ ; at other wavenumbers between 1788 and 1585  $\text{cm}^{-1}$  it may be double this amount.

The source of the intrinsic absorption coefficient, apparently due to local lines since it is independent of pressure, is not understood. At 1585  $\text{cm}^{-1}$  we observed approximately 78.5 percent transmittance for Sample C and 67.8 percent transmittance for Sample B after accounting for the  $\text{H}_2\text{O}$  absorption. If we had observed the same transmittances for B and 89.3 percent for Sample C, we would have concluded that there was no intrinsic absorption. The difference 78.5 percent versus 89.3 percent is greater than our estimated error; therefore, we conclude that there is some intrinsic absorption. Spectral curves in this region show no structure other than that due to  $\text{H}_2\text{O}$  lines. If a very weak  $\text{CO}_2$  band occurred in this region, we would expect to see some structure due to the vibration-rotation lines, although the amount of intrinsic absorption is small enough that we cannot rule out this possibility. The apparent intrinsic absorption may result from an impurity, other than  $\text{H}_2\text{O}$ , which has no line structure that would be observed with the spectral resolution used in obtaining the data. It is also possible, although difficult to believe, that errors in correcting for the  $\text{H}_2\text{O}$  absorption account for the apparent intrinsic absorption.

We feel that the upper curve in Fig. 3-5 represents maximum values for  $\kappa(\text{local})$  due to intrinsic absorption by pure  $\text{CO}_2$ . The correct values may be much less if errors were introduced by impurities. Above

approximately  $1780\text{ cm}^{-1}$ , the increase in  $\kappa(\text{local})$  is due to very weak lines which are a part of the band seen near  $1900\text{ cm}^{-1}$  in Fig. 3-3. Between  $1585$  and  $1490\text{ cm}^{-1}$  the pressure-induced absorption is much greater than between  $1585$  and  $1800\text{ cm}^{-1}$ ; it is also enough greater than any intrinsic absorption that none of the latter was detected.

## SECTION 4

### ABSORPTION COEFFICIENTS AND INTEGRATED ABSORPTANCE FOR CO<sub>2</sub> BETWEEN 1885 cm<sup>-1</sup> AND 2132 cm<sup>-1</sup>

The spectral region from 1885 to 2132 cm<sup>-1</sup> contains several CO<sub>2</sub> bands whose strengths have not been determined, although several of the band centers and line positions have been measured, or can be calculated accurately, from available data. (See Ref. 6 for spectral curves and a table of band centers.) The first part of this section deals with experimental data obtained primarily to determine the strengths of the bands and of single branches of some of the bands. Particular attention was given to the Q-branches. The samples contain CO<sub>2</sub> with He added in order to broaden the lines and remove much of the structure so that the observed transmittance  $T$  was approximately equal to the true transmittance  $T'$ . Helium, rather than N<sub>2</sub>, was used as a broadening gas since it is difficult to obtain N<sub>2</sub> which does not contain enough CO impurity to absorb in this region. Furthermore, the extreme wings of He-broadened lines are weaker and thus produce less continuum absorption. Since the absorption coefficient varies over a wide range of values, different absorber thicknesses were used in the different narrow intervals in order to produce transmittances which could be measured accurately.

Throughout most of the region,  $(-1/u)\ln T$  changes slowly with increasing pressure in the range of pressures used, and  $(-1/u)\int \ln T dv$  is essentially independent of pressure if the integration is performed over an interval including several lines. This result implies that most of the absorption within the narrow interval is due to lines centered within the interval. In a few regions,  $(-1/u)\int \ln T dv$  over a narrow interval increases significantly with increasing pressure. These regions occur where the absorption is very weak and a large fraction of it apparently is due to continuum absorption by the wings of stronger lines which are centered several line widths away from the points of observation. In these cases,  $(-1/u)\int \ln T(v) dv$  does not truly represent the integral of the absorption coefficient of the lines centered in the interval. Examples of such regions are at the absorption minima near Q-branches, and particularly near 1945 cm<sup>-1</sup>, 1990 cm<sup>-1</sup> and from 2135 cm<sup>-1</sup> to 2200 cm<sup>-1</sup>.

The strong absorption feature near 2077 cm<sup>-1</sup> can be recorded easily in atmospheric spectra obtained from an aircraft with the sun as a source. The spectral curves shown in Figs. 4-12 to 4-15 provide laboratory data on known samples at 297°K for comparison with field data. Table 4-2 provides the parameters of the samples and values of  $\int A(v) dv$  over several narrow spectral intervals. In order to better simulate air, we added a mixture of 80% N<sub>2</sub> and 20% O<sub>2</sub> as a broadening gas.

TABLE 4-1  
INTEGRATED ABSORPTION COEFFICIENTS FOR CO<sub>2</sub>

Spectral Region (cm <sup>-1</sup> )	$-\frac{1}{u} \int \frac{1}{u} T(\nu) d\nu$ (molecules <sup>-1</sup> cm <sup>2</sup> cm <sup>-1</sup> )	Sample Parameters <sup>a</sup>			
		P (atm)	P (atm)	u (molecules cm <sup>-2</sup> )	L (meters)
1885.0 - 1916.6	32.0 x 10 <sup>-23</sup>	0.334	14.6	272 x 10 <sup>20</sup>	32.9
1916.6 - 1919.4	5.67	0.334	14.6	272	32.9
1919.4 - 1930.0	9.04	1.00	9.98	205	8.26
1930.0 - 1936.6	16.1	1.00	9.98	205	8.26
1936.6 - 1940.6	0.585	1.00	9.98	205	8.26
1940.6 - 1944.0	0.503 x 10 <sup>-23</sup>	1.00	9.98	205 x 10 <sup>20</sup>	8.26
1944.0 - 2030.0	13.7	4.00	9.16	3320	32.9
2030.0 - 2073.4	299	0.334	14.6	68.2	8.26
2073.4 - 2081.4	195	0.101	9.98	20.7	8.26
2081.4 - 2091.0	21.3	0.334	14.6	68.2	8.26
2091.0 - 2095.8	22.1 x 10 <sup>-23</sup>	0.101	9.98	68.2 x 10 <sup>20</sup>	8.26
2095.8 - 2105.8	9.43	0.334	14.6	68.2	8.26
2105.8 - 2109.4	5.42	0.334	14.6	68.2 x 10 <sup>20</sup>	8.26
2109.4 - 2111.2	2.22	0.334	14.6	68.2	8.26
2111.2 - 2114.8	4.91	0.334	14.6	68.2	8.26
2114.8 - 2126.6	9.32 x 10 <sup>-23</sup>	0.334	14.6	68.2 x 10 <sup>20</sup>	8.26
2126.6 - 2131.8	11.6	0.334	14.6	68.2	8.26
2131.8 - 2191.7	30.6	4.00	9.16	3320	32.9

<sup>a</sup> Sample parameters refer to the samples that were used in determining the integrated absorption coefficient. The samples consist of p atm of CO<sub>2</sub> with helium added to produce total pressure P.

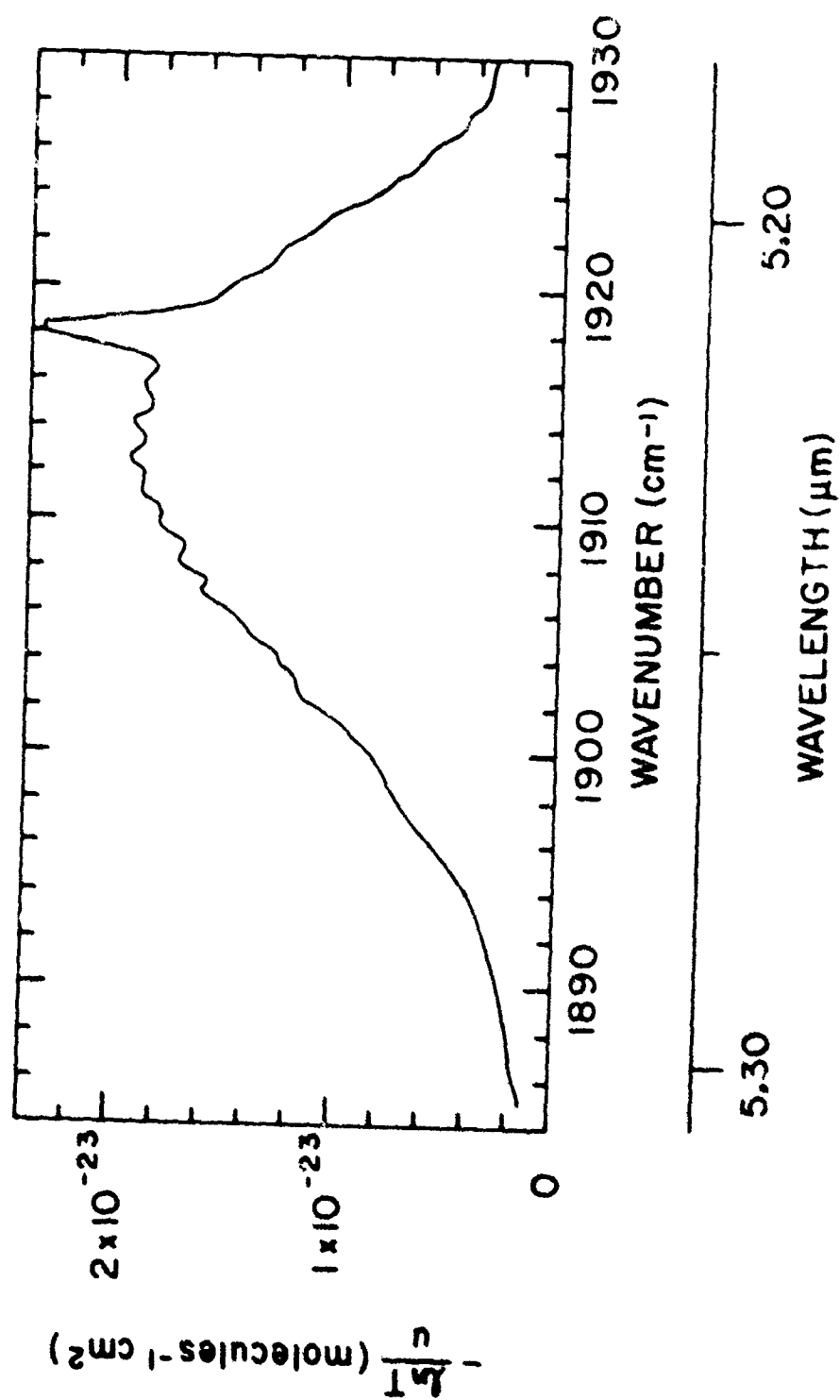


FIG. 4-1. Spectral Curve of  $(-I/I)/u$  for CO<sub>2</sub> from 1884 to 1930 cm<sup>-1</sup>.

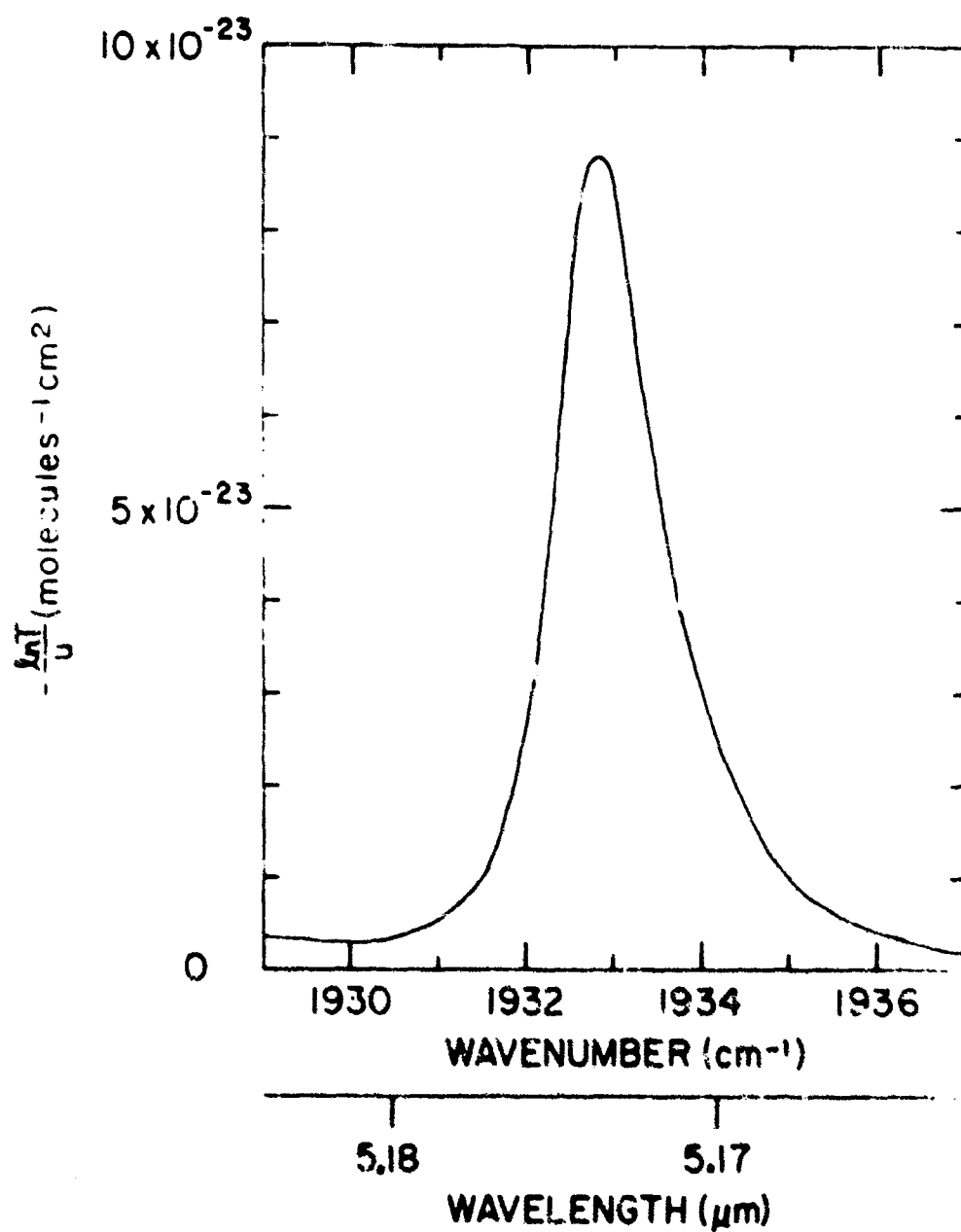


FIG. 4-2. Spectral Curve of  $(-L_\lambda T)/u$  for  $\text{CO}_2$  from 1929 to 1937  $\text{cm}^{-1}$ .



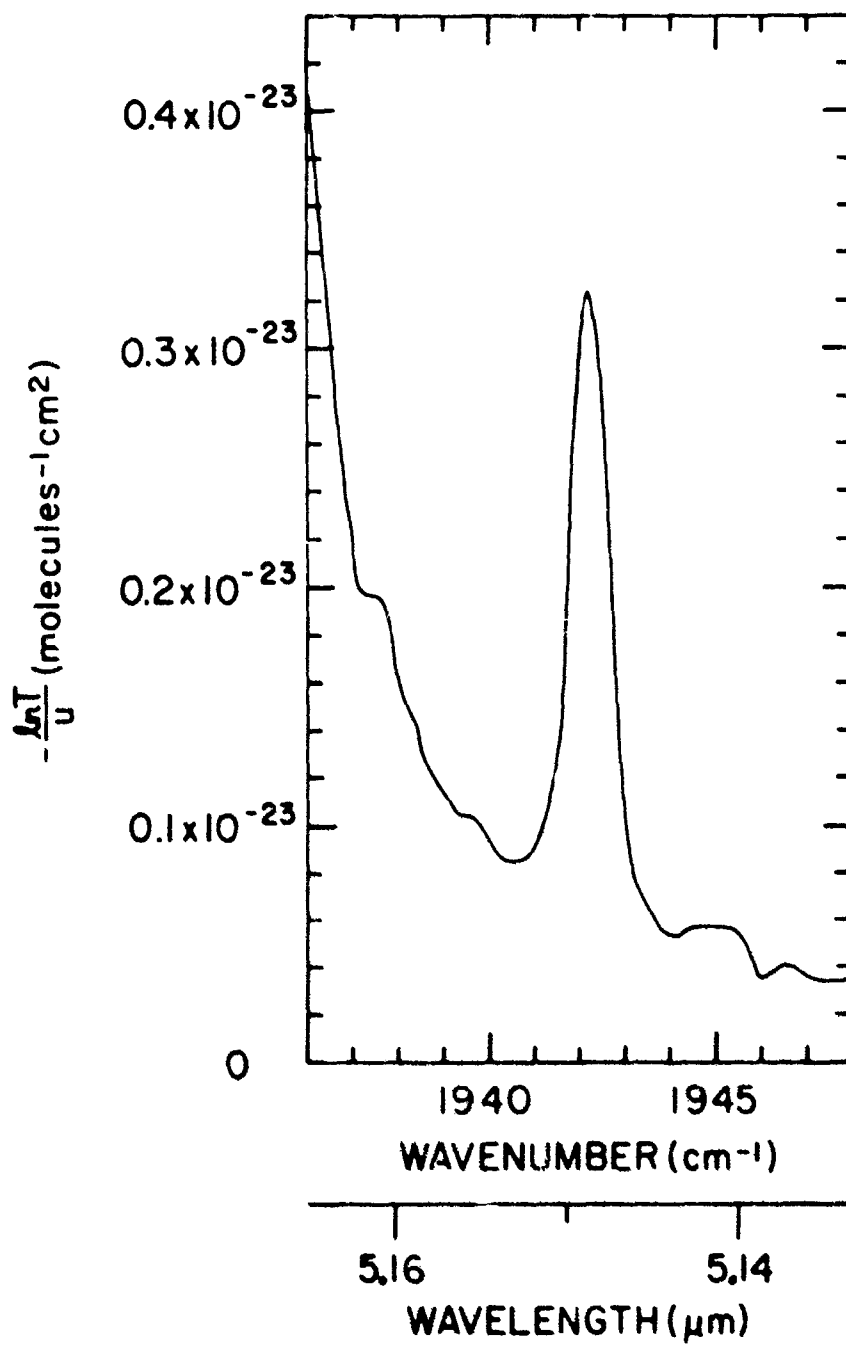


FIG. 4-3. Spectral Curve of  $(-\ln T)/u$  for CO<sub>2</sub> from 1936 to 1948 cm<sup>-1</sup>.

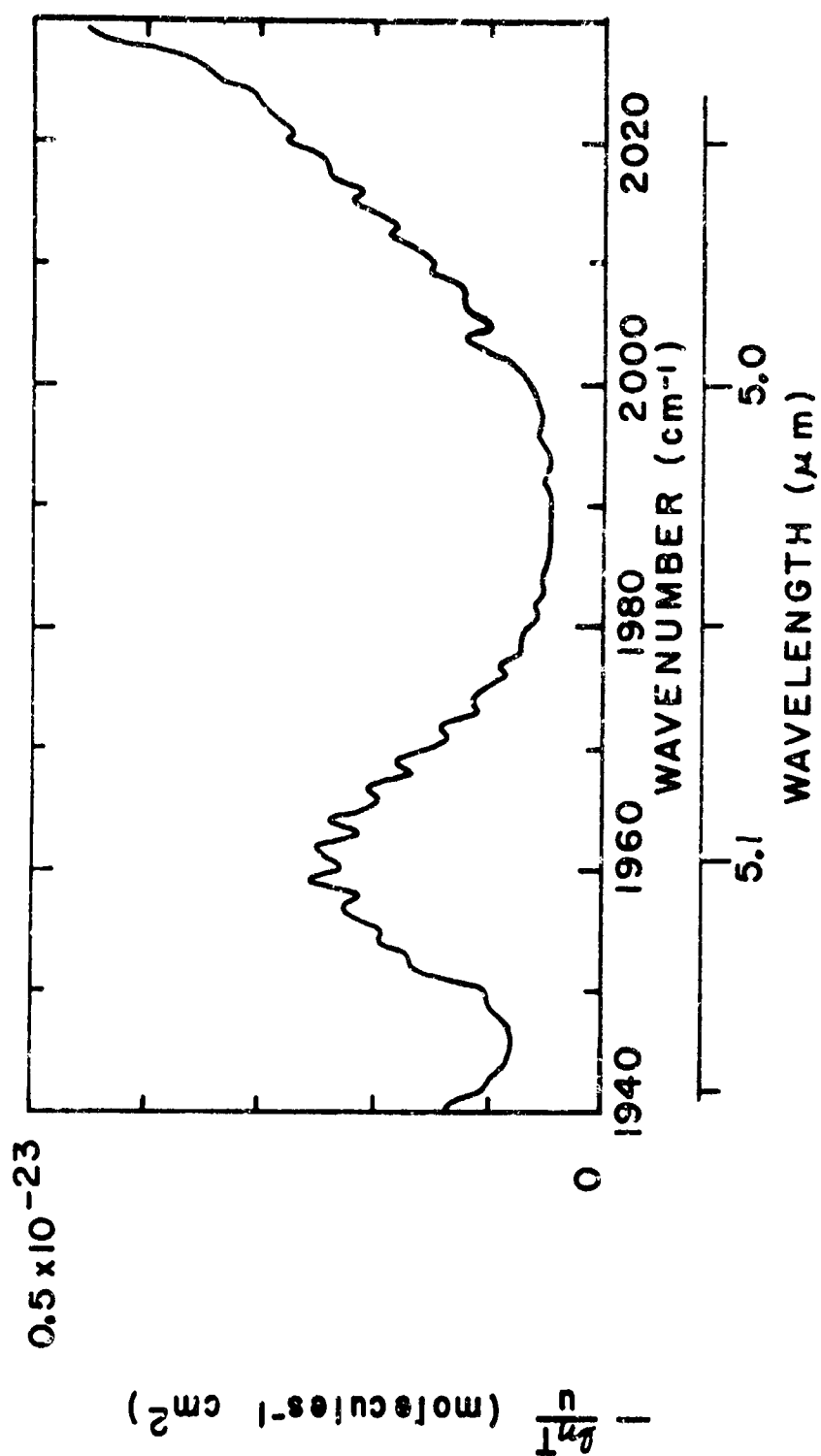


FIG. 4-4. Spectral Curve of  $(-dI/I)/d\lambda$  for CO<sub>2</sub> from 1940 to 2030 cm<sup>-1</sup>.

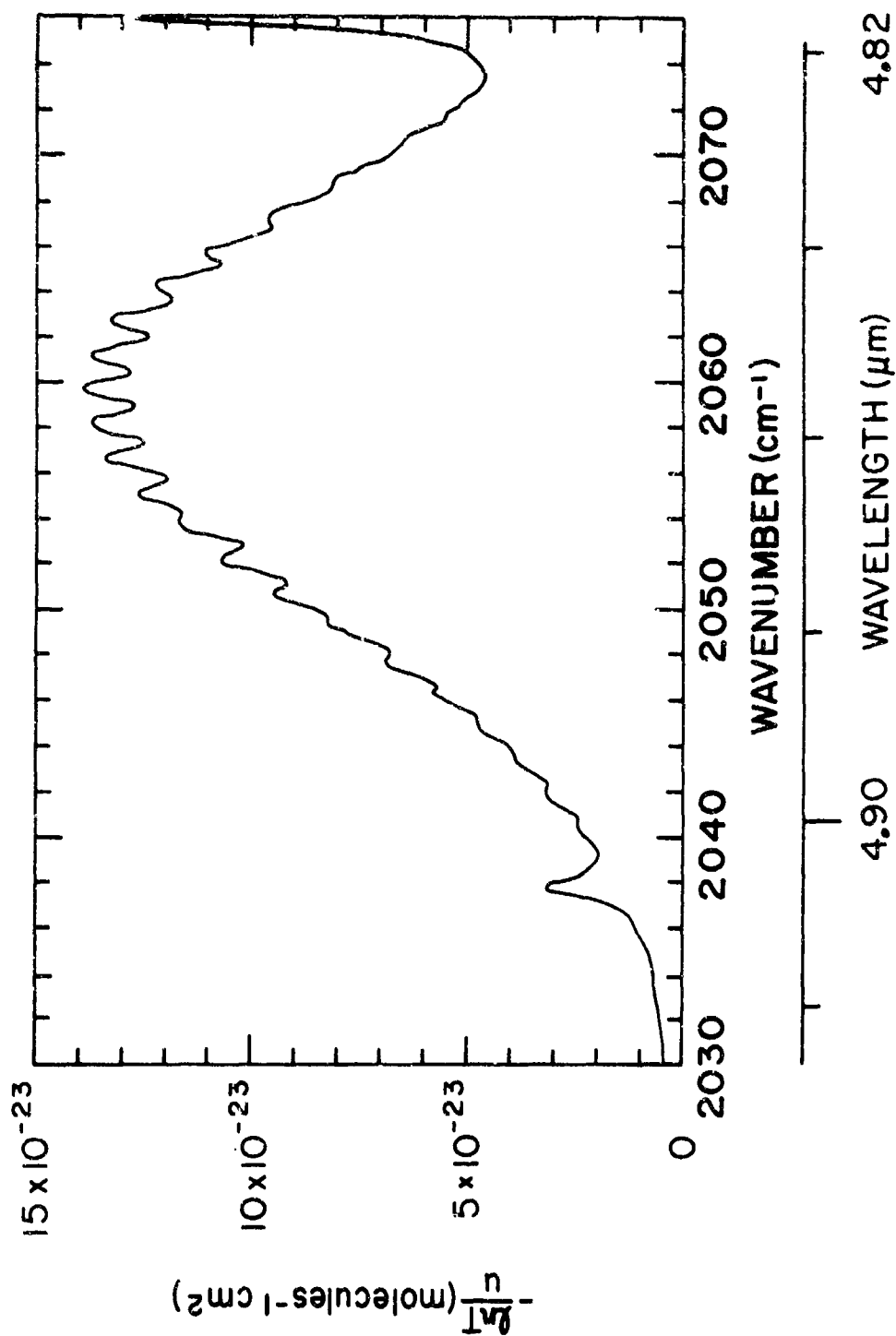


FIG. 4-5. Spectral Curve of  $(-\ln T)/u$  for CO<sub>2</sub> from 2030 to 2076  $\text{cm}^{-1}$ .

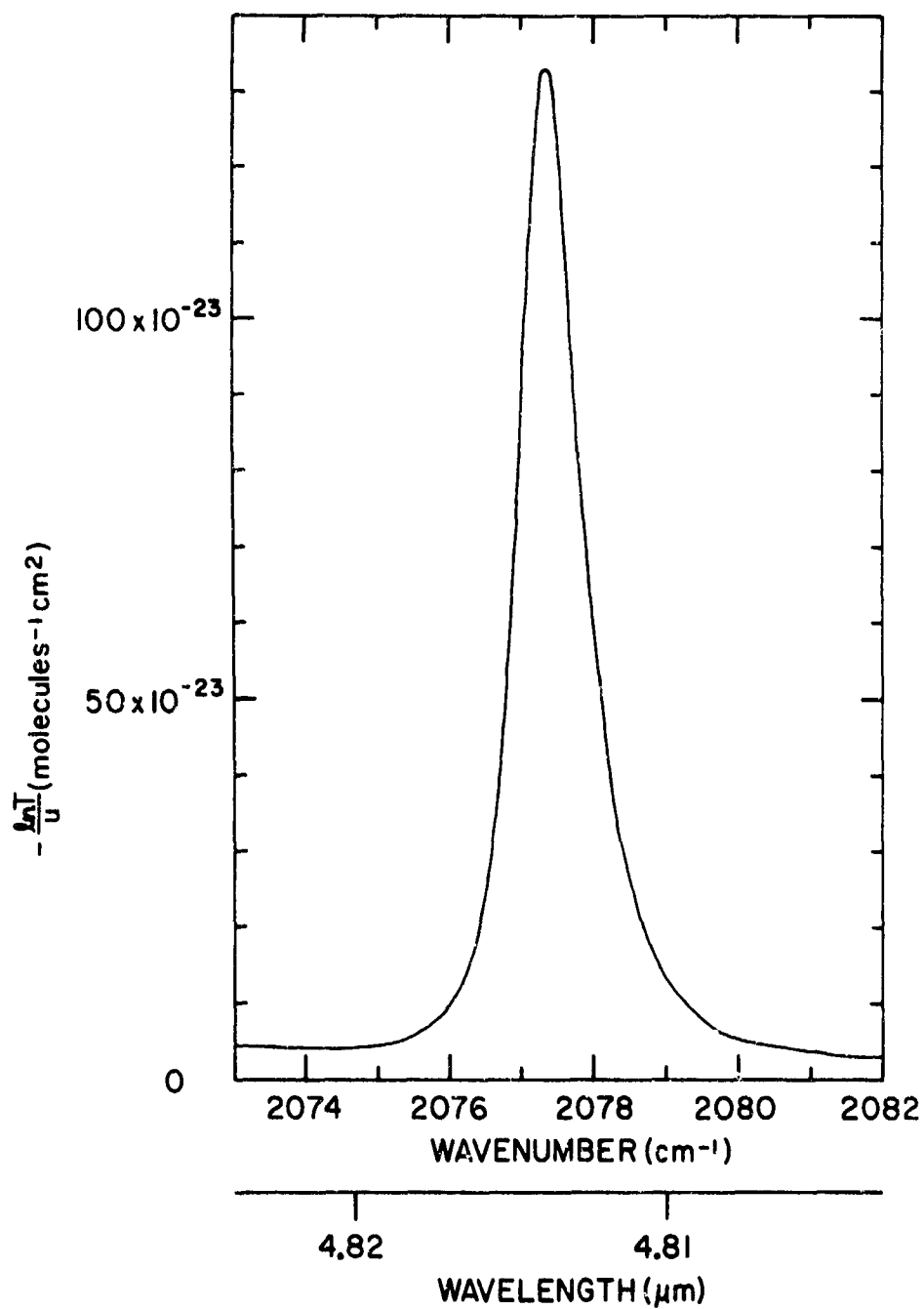


FIG. 4-6. Spectral Curve of  $(-\ln T)/u$  for  $\text{CO}_2$  from 2073 to 2082  $\text{cm}^{-1}$ .

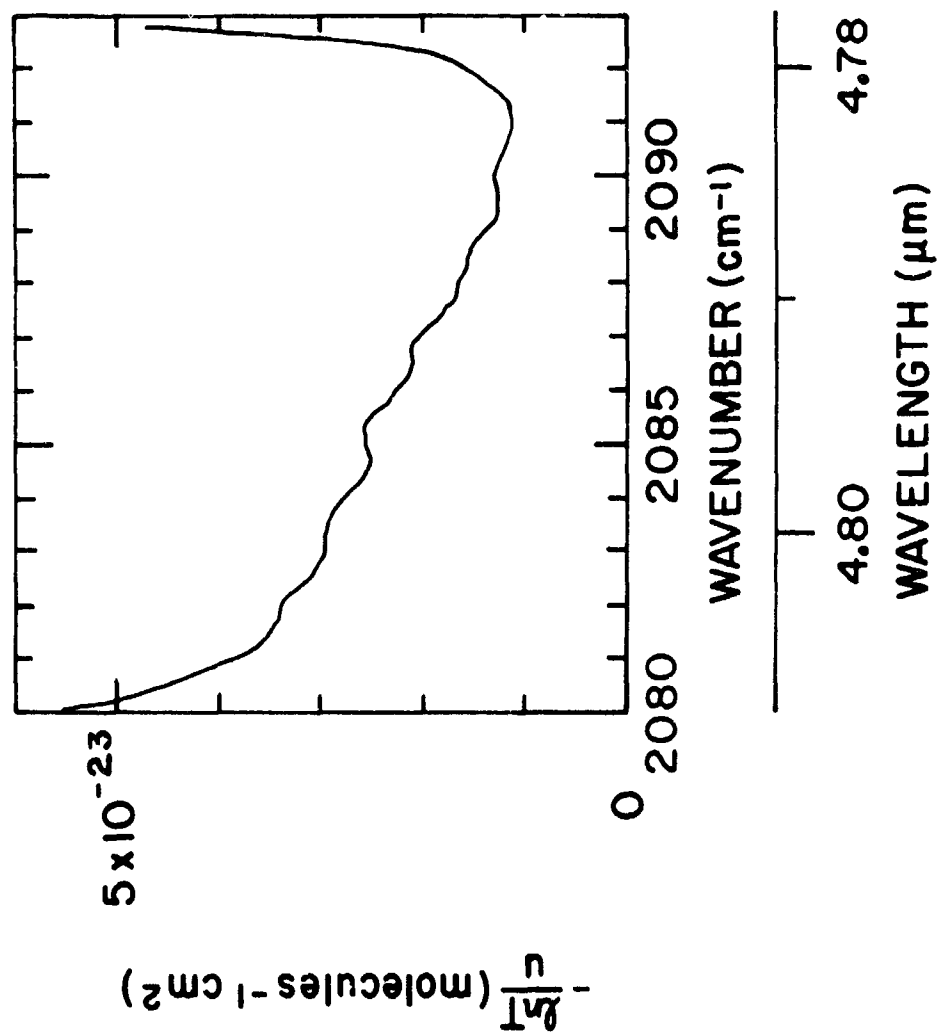


FIG. 4-7. Spectral Curve of  $(- \ln I/I_0)/u$  for CO<sub>2</sub> from 2080 to 2093 cm<sup>-1</sup>.

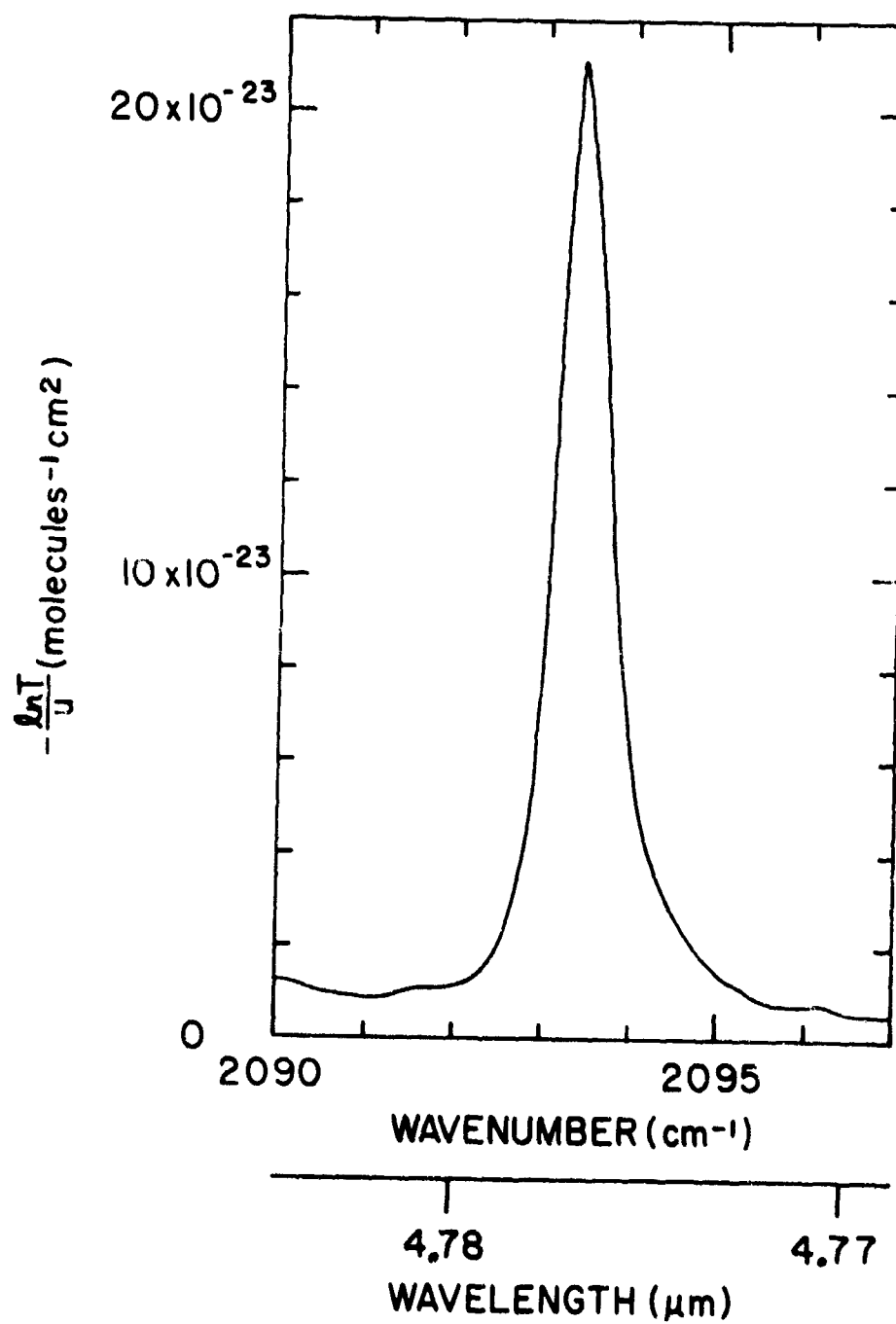


FIG. 4-8. Spectral Curve of  $(-\ln T)/u$  for CO<sub>2</sub> from 2090 to 2097 cm<sup>-1</sup>.

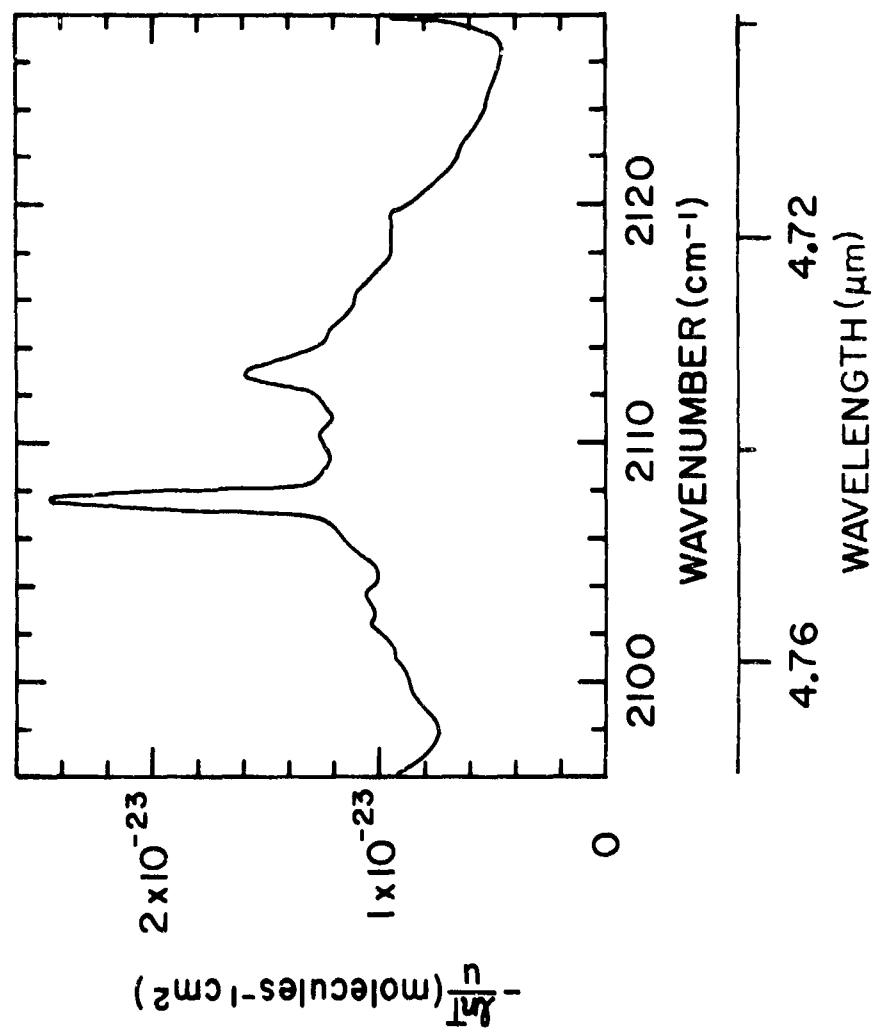


FIG. 4-9. Spectral Curve of  $(- \ln T)/u$  for CO<sub>2</sub> from 2096 to 2128 cm<sup>-1</sup>.

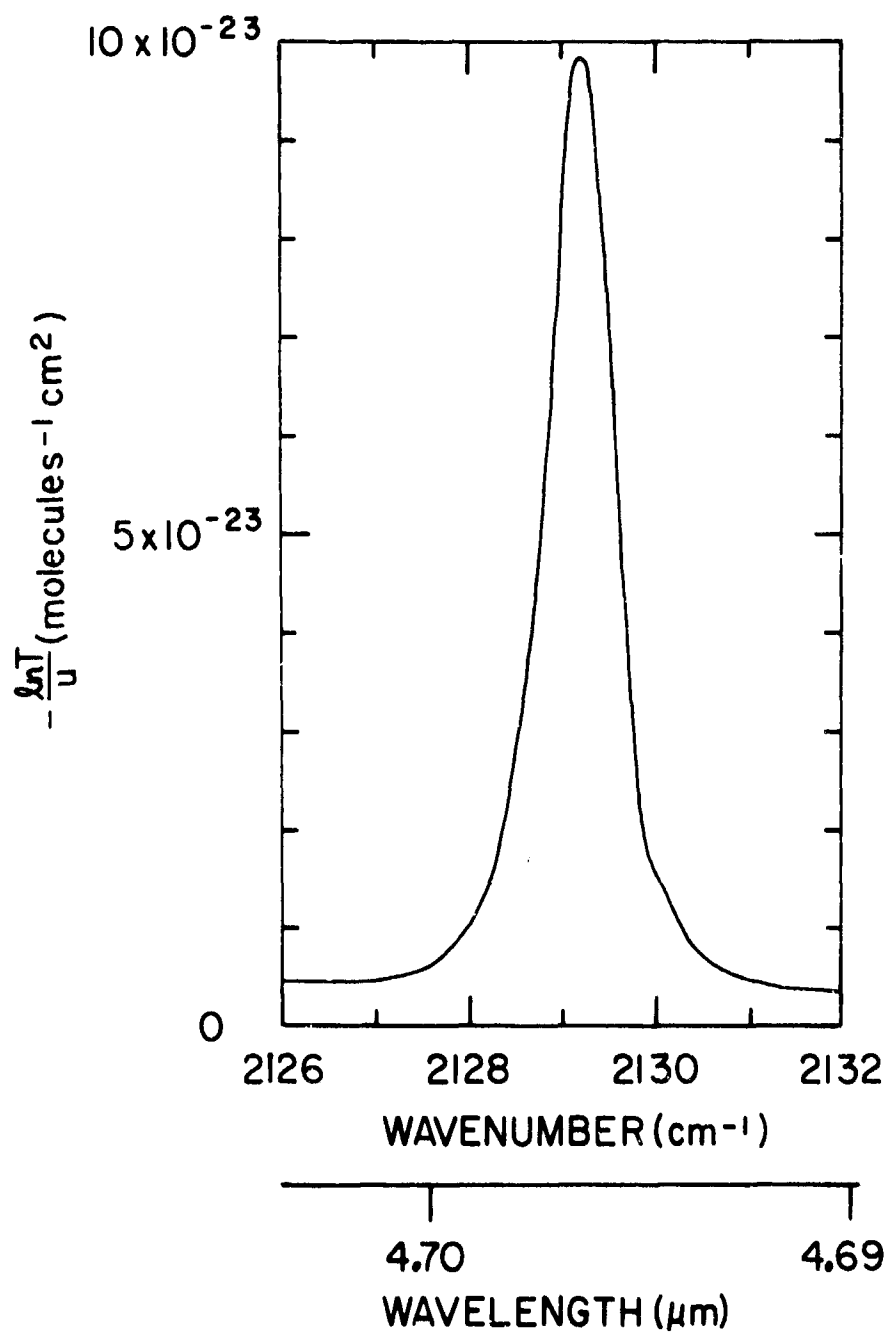


FIG. 4-10 Spectral Curve of  $(-\ln T)/u$  for  $\text{CO}_2$  from 2126 to 2132  $\text{cm}^{-1}$ .



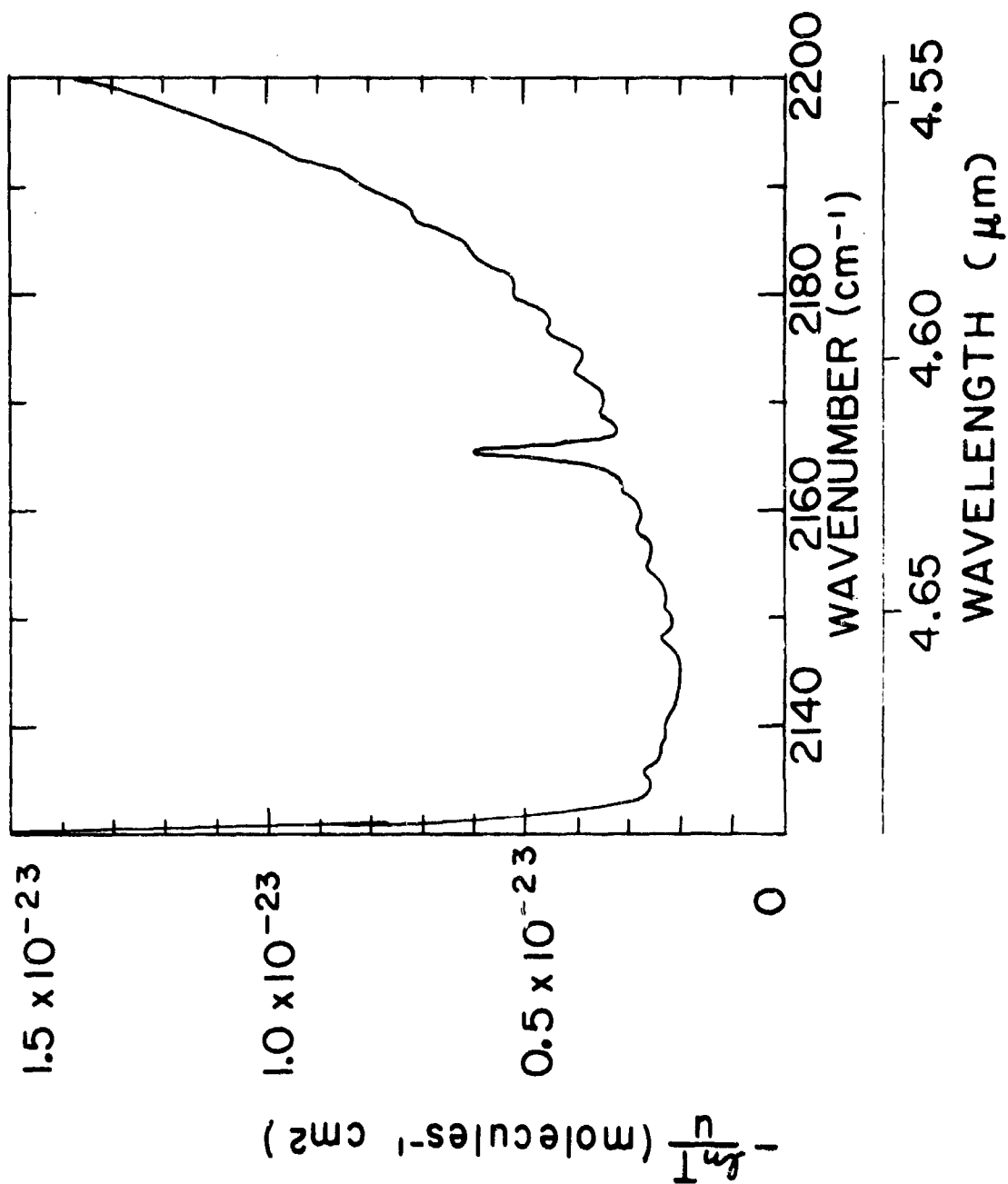


FIG. 4-11. Spectral Curve of  $(-\ln T)/u$  for  $\text{CO}_2$  from 2130 to 2200  $\text{cm}^{-1}$ .

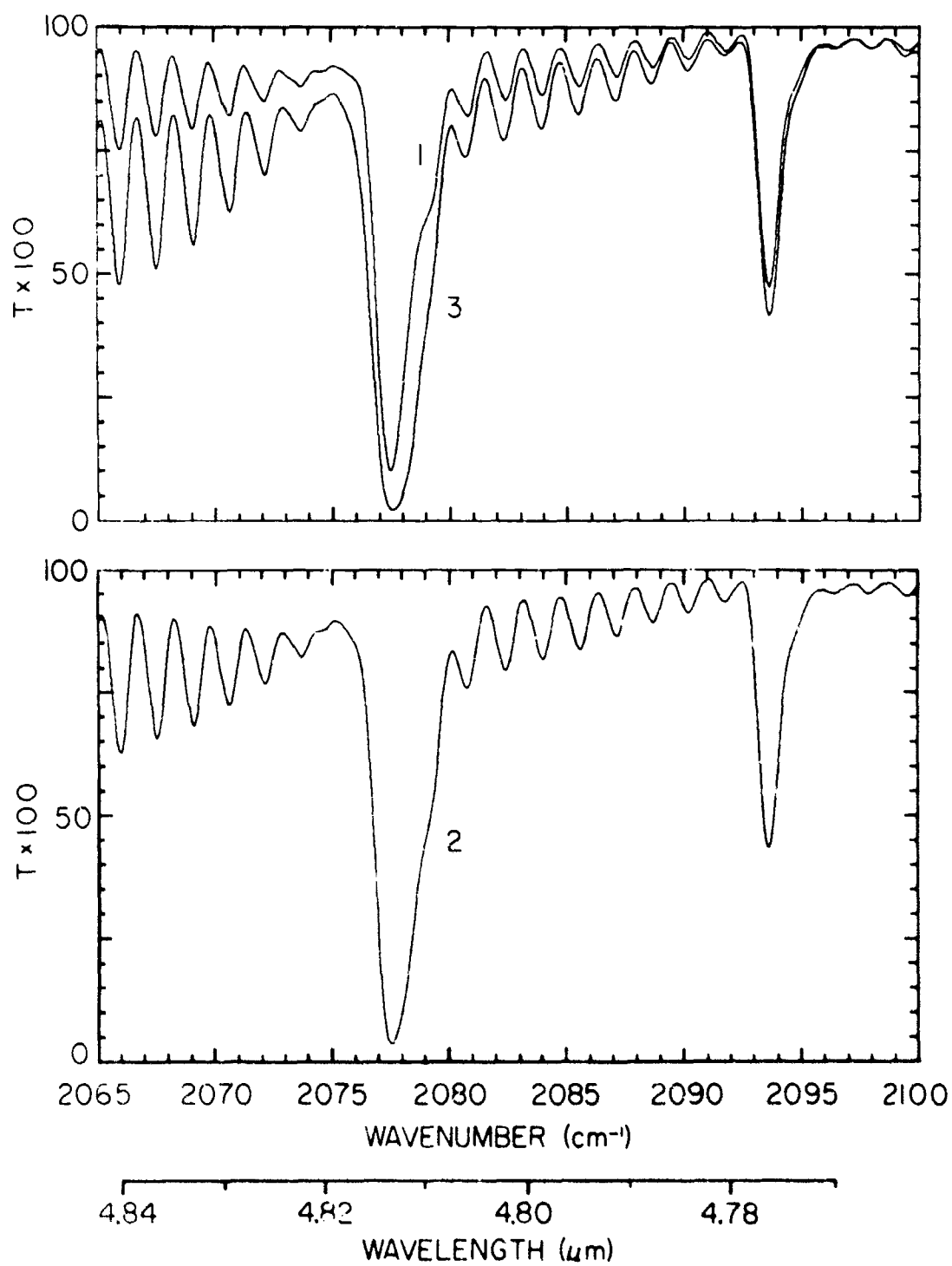


FIG. 4-12. Spectral Curves of Transmittance for CO<sub>2</sub> from 2065 to 2100 cm<sup>-1</sup> for Samples 1, 2, and 3. See Table 4-2 for sample parameters and  $\int A(\nu) d\nu$ .

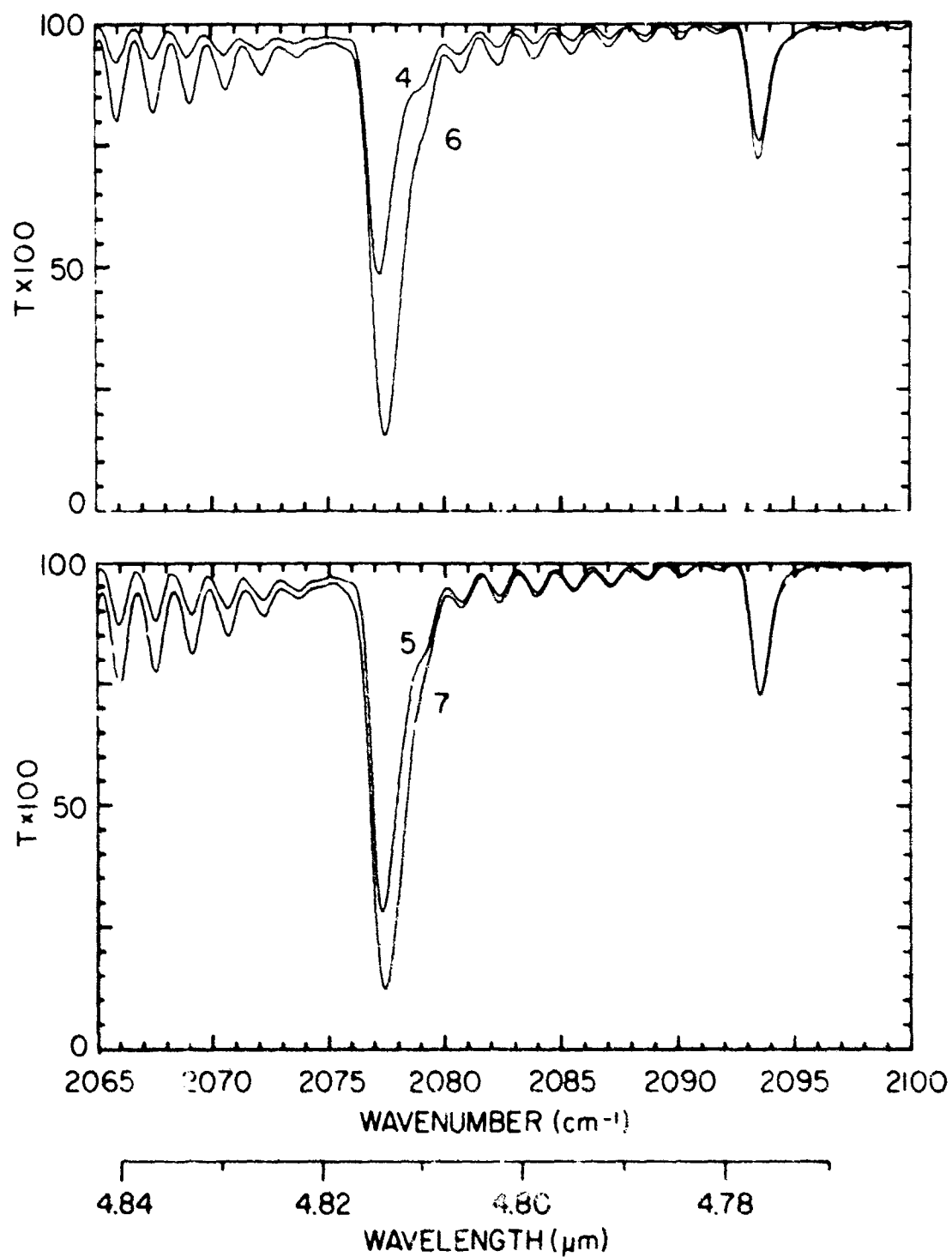


FIG. 4-13. Spectral Curves of Transmittance for  $\text{CO}_2$  from 2065 to 2100  $\text{cm}^{-1}$  for Samples 4, 5, 6, and 7.

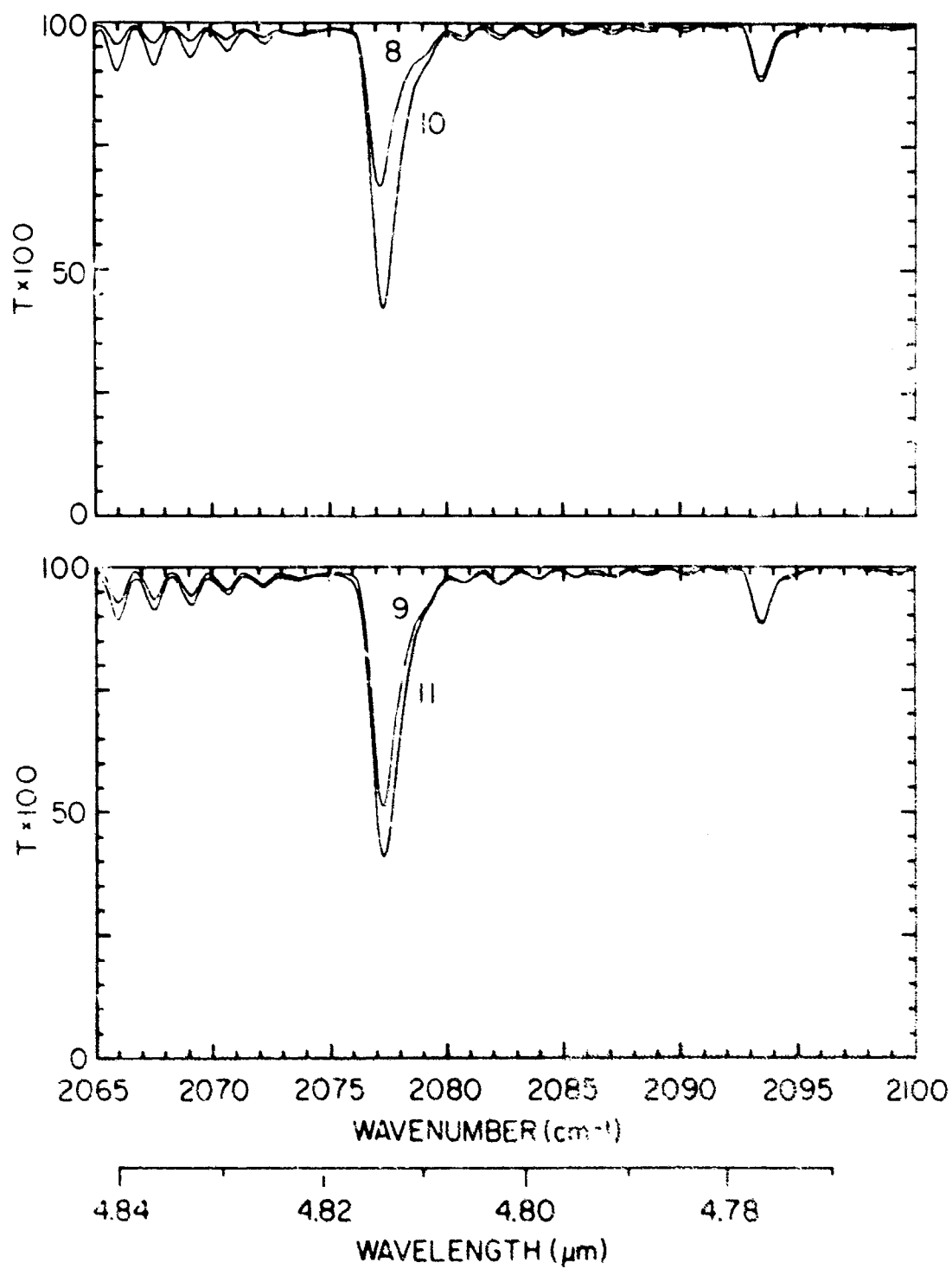


FIG. 4-14. Spectral Curves of Transmittance for  $\text{CO}_2$  from 2065 to 2100  $\text{cm}^{-1}$  for Samples 8, 9, 10, and 11.

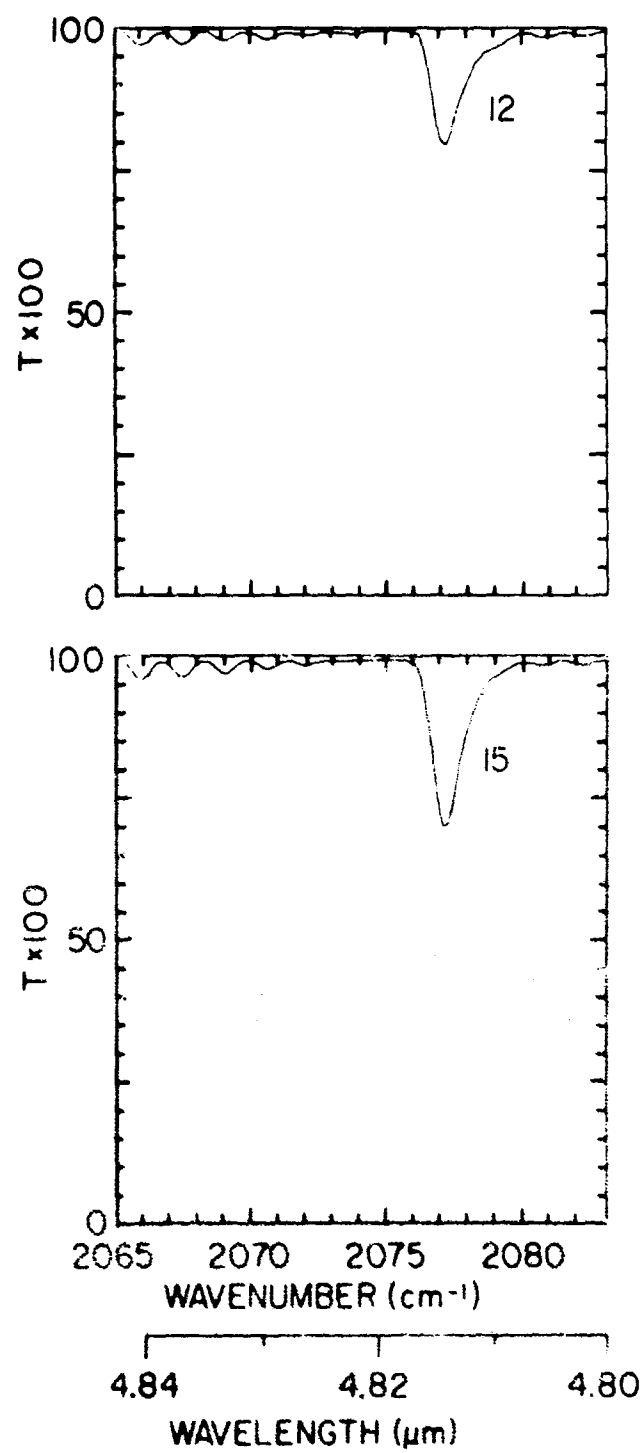


FIG. 4-15. Spectral Curves of Transmittance for  $\text{CO}_2$  from 2065 to 2183  $\text{cm}^{-1}$  for Samples 12 and 15.

## Table 4-2

[illegible]

## SECTION 5

### TRANSMITTANCE DATA STORED ON MAGNETIC TAPE

Under a previous contract, NOmr 3560(00), our laboratory published a series of reports dealing with the absorption of infrared radiation by  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Each report is limited to a given spectral interval and contains detailed information on the absorption by several samples covering a wide range of pressures and path lengths. Tables of the integrated absorptance,  $\int A(\nu) d\nu$ , are included in all of this series of reports; some also include extensive tables of transmittance. As a result of requests from several workers in the field, we have compiled the transmittance tables on magnetic tapes which will be available through Air Force Cambridge Research Laboratories. The transmittance is tabulated versus wavenumber, and enough values are given so that the original spectral curves can be reconstructed without loss of structure by plotting the tabulated values and joining them with straight lines.

Table 5-1 summarizes the data saved on magnetic tape. The report number is the publication number assigned to the report by Aeronutronic. The absorbing gas and the spectral interval covered by the report are included in the table. A given file on the magnetic tape is devoted to the data from a single report.

TABLE 5-1

## SUMMARY OF DATA SAVED ON MAGNETIC TAPE

Report Number	Absorbing Gas	Spectral Interval	
		$\text{cm}^{-1}$	$\mu\text{m}$
U-3704	H <sub>2</sub> O	5,045 - 14,485	0.69 - 1.98
U-3202	H <sub>2</sub> O	2,800 - 4,500	2.22 - 3.57
U-3200	CO <sub>2</sub>	8,000 - 10,000	1.00 - 1.25
U-3930	CO <sub>2</sub>	7,125 - 8,000	1.25 - 1.40
U-3127	CO <sub>2</sub>	6,600 - 7,125	1.40 - 1.52
U-3201	CO <sub>2</sub>	5,400 - 6,600	1.52 - 1.85
U-2955	CO <sub>2</sub>	4,500 - 5,400	1.85 - 2.22
U-4132	CO <sub>2</sub>	3,100 - 4,100	2.44 - 3.22
U-3857	CO <sub>2</sub>	1,800 - 2,850	3.5 - 5.6



## SECTION 6

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13. ABSTRACT From spectral transmittance curves of very large samples of CO <sub>2</sub> we have determined coefficients for intrinsic absorption and pressure-induced absorption from approximately 1130 cm <sup>-1</sup> to 1835 cm <sup>-1</sup> . Most of the pressure-induced absorption arises from the forbidden $\nu_1$ and $2\nu_2$ bands of the <sup>16</sup> O <sup>16</sup> C <sup>12</sup> O <sup>18</sup> molecule. Curves of the absorption coefficients for samples of CO <sub>2</sub> pressurized to approximately 10 atm, or more, with He are presented throughout most of the region from 1885 cm <sup>-1</sup> to 2132 cm <sup>-1</sup> . These curves and a table of the integrated absorption coefficient are adequate to determine the strengths of most of the bands of significance in this region. Spectral transmittance curves of CO <sub>2</sub> absorption between approximately 2065 cm <sup>-1</sup> and 2100 cm <sup>-1</sup> are presented for a variety of samples. Curves of the pressure-induced absorption by N <sub>2</sub> are presented for the 2400-2650 cm <sup>-1</sup> region.			

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14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	<p>N<sub>2</sub></p> <p>CO<sub>2</sub></p> <p>Continuum</p> <p>Absorption</p> <p>Atmospheric Transmission</p> <p>Pressure-Induced Absorption</p>						

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